# THERMODYNAMIC PROPERTIES OF SOME MOLTEN SALT MIXTURES FROM E.M.F. MEASUREMENTS

by

MALCOLM STUART WHITE, M.Sc. (N.Z.)

submitted in fulfilment of the requirements
for the Degree of
Doctor of Philosophy

UNIVERSITY OF TASMANIA
HOBART

(May 1965)

Except as stated therein the thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and that, to the best of my knowledge and belief, the thesis contains no copy or paraphrase of material previously published or written by another person, except when due reference is made in the text of the thesis.

(M. S. WHITE)

CONTENTS

## ABSTRACT

Electromotive force measurements have been completed on formation cells of the type:

$$A(l)/AX_2(l) + MX(l)/C, X_2(g)$$

where $AX_2$ is a molten divalent metal halide and MX a molten alkali metal halide. The following systems have been investigated:

binary; $PbBr_2$-MBr (M = K, Rb, Cs), $PbCl_2$-CsCl

ternary; $PbCl_2$-CsCl-MCl (M = Li, Na, K, Rb)

reciprocal; $CdX_2$-NaY (X = Br or Cl, Y = Cl or Br)

The thermodynamic properties of the components have been discussed in terms of complex ion formation, association of the standard state (the pure divalent metal halide, $AX_2$) and the influence of the alkali metal ion, $M^+$, on the stability of the complex ions.

Activity models have been postulated to explain the deviations of the activity of $AX_2$ from the ideal Temkin activity.

# CHAPTER 1

# INTRODUCTION

## 1.1 ELECTROLYTE SOLUTIONS

Gases at the ideal approximation approached at high temperatures and low densities, are characterized by complete randomness on the molecular scale. The ideal crystal at the other extreme is completely ordered. Mathematically the two extremes of order and disorder can be treated rather simply. Liquids however, are intermediate between the two and have had no comprehensive theory derived. In an ideal gas, the molecules move independently of one another and the energy of the system is simply the sum of the energies of the constituent entities. The case of solids is the converse: translational effects are negligible and the system is constrained by strong forces between the particles (ions, atoms, etc.). For the liquid, the cohesive forces are sufficiently strong for the condensed state to be maintained but not sufficiently strong to prevent translational motion of the constituent particles. A certain degree of short range order is thereby maintained, in a system of overall long range disorder.

Owing to the prominence given the continuity of state between liquids near the boiling point and gases, in classical physical chemistry, the liquid state has usually been theoretically approached from the vapour and treated as a highly compressed fluid. Recent work on x-ray scattering and electron diffraction has initiated the approach to the liquid state from the highly ordered solid.

This latter treatment is more reasonable for temperatures far removed from the critical temperature, as properties of solids and liquids in the vicinity of the melting point show a greater similarity - see later. It is evident therefore, that the correct approach should be governed by the temperature.

It is generally assumed that for solutions of strong electrolytes, the solute "molecules" are almost completely dissociated into ions; this assumption becomes increasingly valid as dilution increases. On the basis of the simplified model of electrolyte solutions used by Debye and Huckel[1] and Falkenhagen[2], these ions are regarded collectively as a gas dispersed throughout a continuous medium, the free solvent possessing the properties of dielectric constant and viscosity. In aqueous solutions, the interactions between ions and water molecules are considered to give rise to hydration sheaths around the ions; the water molecules are regarded as being rigidly bonded to the ions.

For solutions more concentrated than those to which the Debye-Hückel theory applies, the interaction energy between the solute and solvent species becomes of greater importance. The theory of aqueous electrolyte solutions has been extended to solutions of

---

1. Debye and Hückel: Physik. Z., 24 305 (1923)

2. Falkenhagen: Electrolytes (English translation) Intern. Ser. Monographs, Oxford (1934)

greater concentration, by Robinson and Stokes[1], Fuoss[2] and other workers[3-5]. If the range of concentrated solutions is extended to the extreme, in other words to the pure solute, then the shielding effect of water molecules is no longer present.

Molten salts, which may be regarded as a special class of electrolyte solutions, are in effect pure liquids, consisting of ions and in some cases an additional small proportion of undissociated molecular species (see later). This ionic nature is suggested by the fact that molten salts are in general, excellent conductors of electricity. For example, the specific conductance of KCl at 800°C is approximately 22 times that of its molar aqueous solution at 20°C[6].

In consideration of the molten alkali halides, which are perhaps the simplest representatives of this class of fluids, the mutual attraction between unlike charges will cause each cation to be surrounded by a group of anions as nearest neighbours and vice versa for the anions. At the same time, the repulsion between like charges will cause cations (and similarly anions) to be mutually

---

1. Robinson and Stokes: J. Am. Chem. Soc., 70 1870 (1948)
2. Fuoss and Kraus: J. Am. Chem. Soc., 55 3614 (1933)
3. Onsager: Physik. Z., 28 277 (1927)
4. Brunauer, Emmett and Teller: J. Am. Chem. Soc., 60 309 (1938)
5. Bockris: Quart Revs., 3 173 (1949)
6. Bloom and Bockris: Fused Salts, ed. Sundheim, McGraw Hill Book Co., (1964)

repelled. This leads to a more expanded structure than in normal aqueous electrolytes[1]. Apart from electrical conductance however, simple ionic salts are not radically different from other liquids when all are compared at corresponding temperatures[2]. If for example, the properties of molten sodium chloride and water are compared at the same relative temperatures above the melting points, (i.e. $\theta = T/T_{M.Pt.} = 1.06$) then a marked similarity is apparent (see Table 1.1). Although the density and surface tension of fused NaCl is larger by a factor of 1.5, the viscosities of the two liquids are very nearly the same. On the other hand, the low vapour pressure and high surface tension of fused NaCl reflect strong cohesive forces within the liquid.

TABLE 1.1

Properties of water and molten NaCl ($\theta = 1.06$)

| Property | NaCl (850°C) | $H_2O$ (16°C) |
|---|---|---|
| Surface tension (dynes/cm.) | 110.8[3] | 73.3[4] |
| Viscosity (centipoise) | 1.20[5] | 1.11[4] |
| Density (gms./ml.) | 1.5295[6] | 0.9989[4] |
| Vapour pressure (mm. Hg) | 0.89[7] | 13.63[4] |


1. Bloom: Discuss. Faraday Soc., 32 7 (1961)
2. Reddy: Electrochem. Technol., 1, 325 (1963)
3. Bloom, Davis and James: Trans. Faraday Soc., 56 1179 (1960)
4. Hdbk. Chem. and Phys., 35th ed., Chem. Rubber Co., Cleveland (1953)
5. Lorenz: Z. Physik. Chem., (Leipzig) 79 63 (1912)
6. Van Artsdalen and Yaffe: J. Phys. Chem., 59 118 (1955)
7. Barton and Bloom: J. Phys. Chem., 60 1413 (1956)

In dealing with molten salts as liquids, the general difficulties of an exact interpretation of the liquid state is met. The molten salts, not too far from the melting point, exhibit short range structure similar to that of the solid lattice but lack the long range order of the solid (see Section 1.4a). It has been shown, from the analysis of radial distribution functions, that surrounding each reference ion is a shell of other ions with co-ordination number between 3 and 11, very nearly the same as in the solid[1-6]. Outside this sphere the highly ordered structure is lost but a second co-ordination shell is detectable and there is evidence for a third. This provides the greatest difference between the structure of ionic liquids such as molten salts and molecular liquids, as the ordered arrangement provided by the ionic entities is not present for uncharged species.

---


1. Bloom and Bockris: Mod. Aspects of Electrochem., No. 2, ed. Bockris, Butterworth Sci. Pubs., (1959)
2. Harris, Wood and Ritter: J. Am. Chem. Soc., 73 3151 (1951)
3. Wood and Ritter: J. Am. Chem. Soc., 74 1760, 1763 (1952)
4. Lark-Horowitz and Miller: Phys. Rev., 49 418 (1936); 51 61 (1937)
5. Danilov and Krasnitskii: Doklady Akad. Nauk. S.S.S.R., 101 661 (1955)
6. Zernike and Prins: Z. Physik 41 184 (1927)

## 1.2 THEORY OF LIQUIDS APPLICABLE TO MOLTEN SALTS

### a) Free volume models

The concept of free volume developed by Eyring[1] and co-workers and by Lennard-Jones and Devonshire[2], is defined in terms of the Gibbs phase integral $Z_N$, in the configuration space of N molecules, by the relation[3]:

$$Z_N/N! = e^N V_f^N \exp.\ (-(E_N)_{Av.}/kT) \qquad (1.1)$$

where $V_f$ is the free volume and $(E_N)_{Av.}$, the mean potential energy. The free volume is calculated without reference to the exact Gibbs theory by means of models, in which each molecule is supposed to execute gas-like thermal motion in a cage formed by the average intermolecular force field of its neighbours.

Qualitatively this free volume may be defined as the difference between the total volume available for movement of the particles within their cages and the volume of the particle. To overcome limitations of this model, e.g., failure to interpret the entropy of fusion[4], Cohen and Turnbull[5] introduced a modified concept of free volume. They considered the free volume to be no longer associated uniformly with each cell, the contribution per cell being distributed thermally. The "liquid" free volume for molecular

---

1. Eyring and Hirschfelder: J. Phys. Chem., 41 249 (1937)
2. Lennard-Jones and Devonshire: Proc.Roy.Soc., A163 53 (1937), A165 1 (1938)
3. Kirkwood: J. Chem. Phys., 18 380 (1950)
4. Bloom and Bockris: Fused Salts, ed. Sundheim, McGraw Hill Book Co. (1964)
5. Cohen and Turnbull: J. Chem. Phys., 31 1164 (1959)

liquids is defined as:

$$v = \bar{v} - v_o \qquad (1.2)$$

where $\bar{v}$ is the average volume per molecule (referred to the whole liquid) and $v_o$ is the volume per mole when the cells correspond to those in which the molecule would be in a hypothetical solid at the same temperature. In this case it is assumed that above a certain temperature non-energetic distribution of liquid free volume can occur in the liquid because of equal and opposite energy changes due to expansions and compensating contractions of pairs of cells[1]. This redistribution of free volume may give rise to the required entropy term[2].

b) Quasi-lattice and Hole theories

In pure liquid electrolytes, the change in molar volume on fusion is 15-25% of the molar volume of the solid[3]. However, the free volume per mole in the liquid alkali halides is about 2% of the molar volume. The change in the free volume*, as deduced from ultrasonic velocity measurements on melting the crystalline solid, cannot therefore account for the total observed change in the molar volume during fusion. The presence of a substantial fraction of holes

---

* The "free volume" as defined by Bockris and Richards - ref. 3

1. Turnbull: G.E. RES. LAB. Reprint, 61-RL-2671M

2. Bloom and Bockris: Fused Salts, ed. Sundheim, McGraw Hill Book Co. (1964)

3. Bockris and Richards: Proc. Roy. Soc., A241 44 (1957)

in the pure liquid must, therefore, be assumed to be present to account for this change. The introduction of such holes in a solid lattice would decrease the mean co-ordination number for unlike ions; e.g. LiCl on melting shows a decrease in the mean co-ordination number from 6 to 5[1,2].

The quasi-lattice model[3,4], assumes the ions to be situated on lattice sites and the holes (also on lattice sites) are regarded as Schottky defects. The hole model[5,6] differs in that it assumes simple molten electrolytes to be constituted by spherical cations and anions, each behaving as independent linear harmonic oscillators, among which are randomly distributed a number of holes.

In the quasi-lattice model, the work of making a vacancy for a cation is assumed to be analagous to the case of the solid lattice[7], i.e:

$$\Delta H_{VAC.} = \tfrac{1}{2}(H_{CAT.} + H_{AN.} - H_{LAT.}) \qquad (1.3)$$

where $H_{CAT.}$ and $H_{AN.}$ are the work required to remove a cation and anion respectively to infinity and $H_{LAT.}$ is the lattice energy.

---


1. Miller and Lark-Horowitz: Phys. Rev., 51 61 (1937)
2. Johnson, Agron and Bredig: J. Am. Chem. Soc., 77 2734 (1955)
3. Frenkel: Acta Physicochim. U.R.S.S., 3 633, 913 (1935)
4. Bresler: Acta Physiochim. U.R.S.S., 10 491 (1939)
5. Altar: J. Chem. Phys., 5 577 (1937)
6. Fürth: Proc. Camb. Phil. Soc., 37 252, 276, 281 (1941)
7. Bloom and Bockris: Fused Salts: ed. Sundheim, McGraw Hill Book Co. (1964)

Although both these models generally apply with relatively good agreement to molten salts, the applicability of the quasi-lattice theory to metallic and molecular liquids is questionable[1-4].

c) Dislocation model

Schottky defects are regarded as diffusing in from the surface of a crystal as the melting point is approached[5]. With increase in concentration these defects condense into dislocations[6] and the free volume produced requires fewer broken bonds than a similar increment of free volume due to isolated vacancies. The rate of formation of vacancies greatly increases as the melting point is approached. This is equivalent[7,8] to a breaking up of the crystal into crystallites with fluctuating boundaries. The heat of fusion predicted by this model should be approximately two orders of magnitude less than the heat of vaporisation[5] because the bulk of the molecules are within crystallites rather than at the dislocations. The model has been justified in a theory pertaining to glasses[9] and in the explanation of small changes in the partial molar volumes of $SiO_2$ in liquid silicates.[10]

---


1. Meyer and Nachtrieb: J. Chem. Phys., 23 1851 (1955)
2. Lawson: Phys. and Chem. Solids, 3 250 (1957)
3. Prokhorenko and Fisher: Zh. Fiz. Khim., 33 1852 (1959)
4. Turnbull: G.E. Res. Lab. Reprint, 61-RL-2671M
5. Rothstein: J. Chem. Phys., 23 218 (1955)
6. Seitz: Phys. Rev., 79 890 (1950)
7. Van der Merwe: Proc. Phys. Soc., (London) A63 616 (1950)
8. Read and Shockley: Phys. Rev., 78 275 (1950)
9. Preston and Turner: J. Soc. Glass Technol., 26 331 (1932)
10. Bockris, Tomlinson and White: Trans. Faraday Soc., 52 299 (1956)

d) Polyhedral hole model

Frank[1] observed that for substances with co-ordination number 12, the particles may be arranged in such a way that each sphere, the spheres being in contact, is situated at a face centre of a dodecahedron. This arrangement provides maximum short range cohesive energy and because spheres cannot be close packed within such a structural arrangement, holes are necessarily introduced. On consideration of a number of possible polyhedral arrangements, Bernal[2] found that some had five-fold symetry which, because of their failure to close pack, contained holes.

It is possible to calculate the mutual energies of interaction between a random assembly of hard spheres by the Lennard-Jones $(A/r^6 + B/r^{12})$ potential equation[2]. From those arrangements of minimal energy, the mean radial distribution functions can be evaluated and these very closely approximate those obtained from the x-ray and neutron diffraction studies on lead and liquid argon[3,4].

---

1. Frank: Proc. Roy. Soc., (London), A215 43 (1952)
2. Bernal: Nature, 185 68 (1960)
3. Furukawa: Nature, 184 1209 (1959)
4. Henshaw: Phys. Rev., 105 976 (1957)

e) Significant structure model

On the basis of this model, a liquid is regarded as consisting of three significant structures[1-3]:

1. The solid-like binding of a molecule to an equilibrium position by its neighbours.
2. Position degeneracy - molecules that can shift to different lattice sites at the price of storing up elastic energy due to structural distortion.
3. The gas-like escape of a molecule from the lattice in at least one direction. The gas-like holes for the application to molten salts are treated as occuring in pairs, to correspond with their experimentally established state in the gas phase at normal pressures.

Although the model has advantages, by using vacancy, crystallite and compressed gas models in the derivation, it has come under criticism in its application[4-6].

---


1. Eyring, Ree and Hirai: Proc. Natl. Acad. Sci., U.S., 44 683 (1958)
2. Fuller, Ree and Eyring: ibid., 45 1594 (1959)
3. Carlson, Eyring and Ree: ibid., 46 333 (1960)
4. Barton and Bloom: J. Phys. Chem., 63 1785 (1959)
5. Blomgren: Ann. N.Y. Acad. Sci., 79 781 (1960)
6. Bloom and Bockris: Fused Salts, ed. Sundheim, McGraw Hill Book Co. (1964)

When comparing experimental data with that calculated theoretically for the quantities: volume change on fusion, entropy change on fusion, coefficient of expansion, compressibility and self-diffusion coefficients, the hole and then perhaps the quasi-lattice model give the best agreement. The significant structure theory gives very good co-relation as far as it has been applied, i.e., to the volume and entropy changes on fusion. The liquid free volume model, is unsatisfactory for all but the volume change on fusion and the crystallite and polyhedral hole models, give qualitative information only.

## 1.3 THE CONCEPT OF MELTING AND COMPLEX IONS

It is an empirical fact[1] that the values of the heat capacity at constant pressure, $C_p$, at temperatures a few degrees below the melting point for the solid, are of the same order in many cases, as the values at temperatures a few degrees above the melting point for the liquid. This indicates that the processes responsible for heat intake, are much the same for the two phases. So far as is known, crystals of the inert gases can exhibit only a single mechanism of melting[2]. This involves extreme positional disorder of the atoms in the melt with respect to an ideal crystal lattice. For the alkali halides, which have been regarded as crystals of inert gas ions, entropies and volume changes on fusion are no longer independent of the ionic radii[3].

The ratio of the number of independent configurations of the liquid, $W_l$, to that of the solid, $W_s$, determines the magnitude of the entropy on melting and may be represented[4] by the equation:

$$S_f = R \ln (W_l/W_s) \qquad (1.4)$$

(This ratio is always greater than unity, implying greater randomness in the liquid.) Ubbelohde[4] has indicated the principal effects of

---

1. Kuhn and Grundmann: Ber., 690 224 (1936)
2. Rhodes and Ubbelohde: Proc. Roy. Soc., A251 156 (1959)
3. Schinke and Sauerwald: Z. anorg. u allgem. Chem., 287 314 (1956)
4. Ubbelohde: Structure of Electrolytic Solns., ed. Hamer, Wiley & Sons inc., (1959)

melting by assuming $S_f$ to be made up of many contributing terms, i.e.

$$S_f = S_{VIB.} + S_{OR.} + S_{POS.} + S_{CONF.} + S_{ASSOC.} \qquad (1.5)$$

where $S_{VIB.}$ is the entropy change due to the possible lowering of vibrational frequencies owing to increased freedom of the ions on melting, (assumed to be small except in the case of premelting)

" $S_{OR.}$ is the entropy change due to increased orientational randomization of non-spherical ions, occuring either below the melting point at temperatures corresponding to lambda points in the solid state, or an expansion due to melting

" $S_{POS.}$ is the entropy increase due to an increase in positional disorder, with respect to the ideal lattice sites. This directly results in an increase in the volume on melting (except in non-ionic crystals), to allow for the greatly increased potential energy of repulsion

" $S_{CONF.}$ is the entropy change due to internal configurational changes (very minor contribution)

" $S_{ASSOC.}$ is the entropy change due to changes in association or chemical bonding on melting. On melting, localized association complexes can be formed as a result of the positional disorder. The dissociation of normally paired groups may also contribute to this entropy term.

In comparing the alkali halides, the volume increase on melting decreases as the cation radius increases, thus substantiating the proposition that the repulsive effects between neighbouring anions contribute largely to the volume increase, especially when $r_+/r_-$ is small. For a given cation, the polarizability of the anion increases as the atomic number increases and this tendency leads to increased association. When cation-anion pairs evaporate from the crystal to the vapour, then the lowered symmetry of the force field tends to give greater association than in the crystal. Although the asymmetrical force fields in the melt are less pronounced, the same effect of ion pair formation will occur in regions of local defective symmetry. This results in an increase in volume on melting, smaller than would be expected from non-elastic spheres[1].

In the melting of ionic crystals containing polyatomic ions, e.g., group I nitrates, there is a comparatively large contribution to the entropy of fusion from the entropy of formation of association complexes, other than simple ion pairs[2]. The symmetry requirement of lattice structures, necessitates the equivalence of attractive forces between any one positive and the appropriate number of negative ion nearest neighbours. This requirement is in opposition to the tendency to form ion pairs and hence larger ion aggregates. Compared with ion pair formation, these larger "complexes" give a still smaller volume increase on melting (e.g. the nitrates studied by Davis et al[2]).

---

1. Ubbelohde: Structure of Electrolytic Solutions, ed. Hamer, Wiley & Sons inc., (1959)

2. Davis, Rogers and Ubbelohde: Proc. Roy. Soc., A220 14 (1953)

It is evident that the requirement for ionic associations or complexion formation, depends upon the asymmetry of the force fields during and after melting. Once formed, the stability of such entities will depend upon two main factors; (1) the nature of the bonding forces between the ions within the species, and (2) the nature and strength of the force fields provided by surrounding ions. The lifetimes of such species will therefore depend on the nature of the melt.

In order to substantiate the presence of such species, they must exist for a period such that their presence can be detected by some physical or chemical property. For pure salts, the presence of associated groups such as ion pairs and complex species can be understood from the point of view of melting mechanisms. Such ions as $SO_4^{2-}$, $CO_3^{2-}$, $NO_3^-$, etc., are well established (see Section 1.4a). The situation is far more complicated for mixtures, as compared to single salts however, where the interacting force fields are both increased in number and also more variable.

Evidence for species other than simple ions has been obtained from the many methods used in the investigations of the nature of molten salts. Of these methods, those involving direct observations, such as x-ray and neutron diffraction and the various spectrographic methods, have yielded perhaps the most significant information. Deviations from ideal values* in thermodynamic,

---

* By "ideal" is meant the values of the property, at different compositions, that are expected if the solution consists of unassociated and non-interacting simple ions.

transport and other properties, have also provided a means for the substantiation of the presence of associated groups. The criterion of non-ideality of systems does not provide unequivocal evidence for complex formation and such evidence must be considered very carefully.

## 1.4 EXPERIMENTAL METHODS WHICH HAVE BEEN USED IN THE INVESTIGATION OF MOLTEN SALTS

### a) Diffraction studies

An elucidation of the detailed structure of a liquid requires more information than that derived from x-ray and neutron diffraction studies. The radial distribution function, which gives the probability that pairs of atoms will be found separated by a given average distance, provides a good qualitative description and coupled with other information can yield a reasonably comprehensive picture.

In a pure simple fused salt (e.g. the alkali halides) there are three different radial distribution functions which describe the cation-anion, cation-cation and anion-anion distributions. From these functions, the nature of the atomic arrangements within the liquid can be infered in so far as the liquid is non-random and each ion is surrounded by an average number of oppositely charged ions. Figure 1.1 shows such a radial distribution curve[1]. The first two maxima at 2.5 and 3.8 $\mathring{A}$, represent interatomic separations which are predominant in the melt and these are assigned to (Li-Cl) and (Cl-Cl and Li-Li) respectively. This assignment is consistent with the theoretical prediction that each ion is preferentially surrounded by ions of opposite charge. The area beneath the peaks, taking into account the

---

1. Levy and Danford: Molten Salt Chemistry, ed. Blander, Interscience (1964)

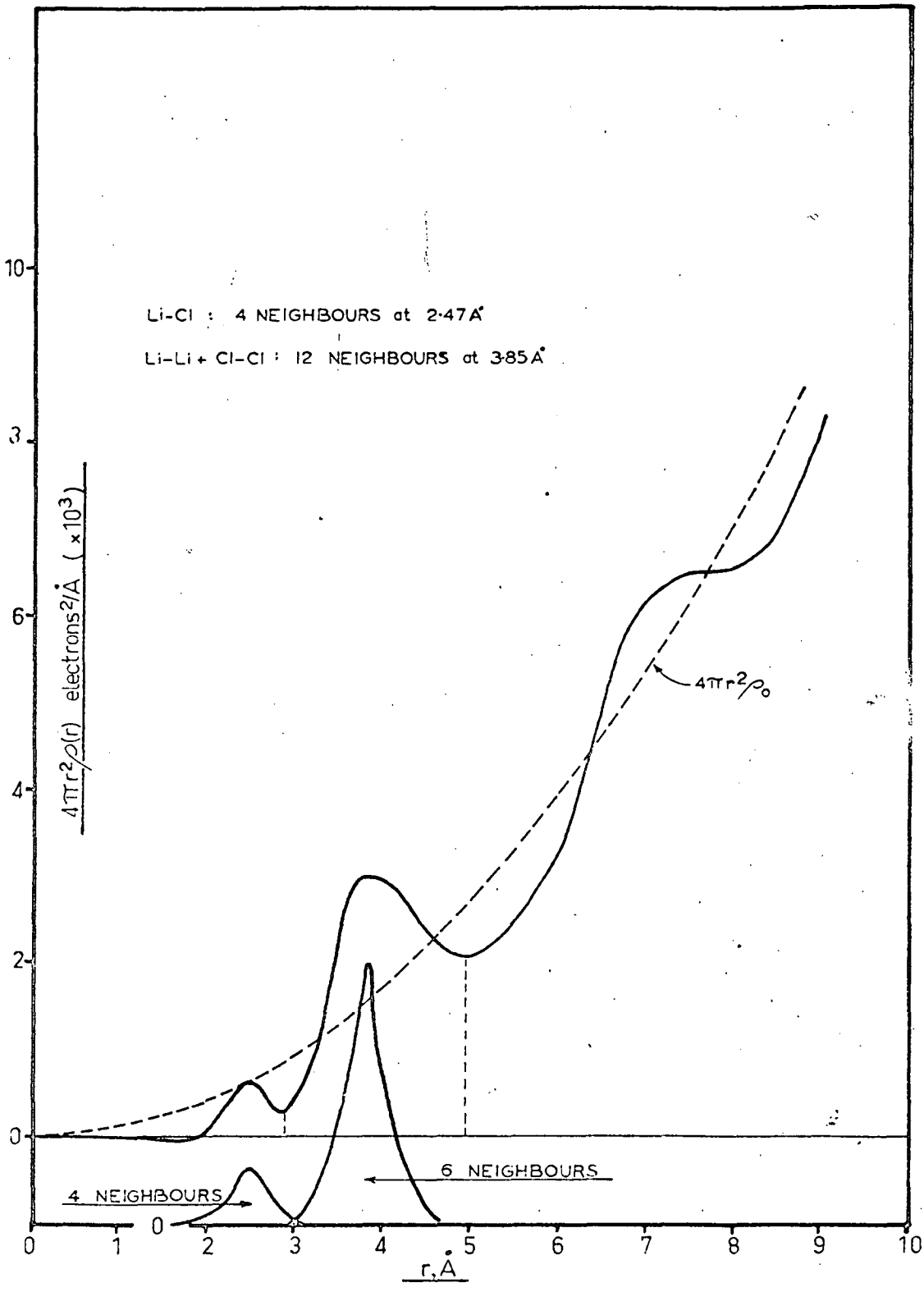



FIG. 1·1 RADIAL DISTRIBUTION CURVE FOR MOLTEN LiCl

inherent uncertainty in estimation, gives the average numbers of nearest neighbours.

For neutron diffraction studies, if the metal atom has a negative nuclear scattering amplitude (chlorine being positive for say $Li^7Cl$), then those regions in which the pair density function for unlike pairs is large, will produce negative fluctuations in the experimental radial distribution curve[1]. This lends confirmation to the theoretical predictions for concentric spherical shells of differing charge.

The corresponding fluctuations for the positive peak in the x-ray radial distribution curve for $Li^7Cl$, is negative at the same distance from the nucleus, i.e., in molten LiCl the nearest neighbours are of unlike charge. Further information suggested by these two curves is that for molten LiCl, unlike ions predominate at the intermediate separations of about 4.5 and 7.5 Å. A similar set of data can be obtained for all the alkali halides[2-6].

It has been found[5,6] that the average number of nearest neighbours among the alkali halide melts is between 3.5 and 5.5, whereas the typical solid structure has a co-ordination number of 6,

---


1. Levy and Danford: Molten Salt Chemistry, ed. Blander, Interscience, (1964)
2. Zarzycki: J. Phys. Radium, 19 13A (1958), 18 65A (1957)
3. Zarzycki: Compt. rend, 244 758 (1957)
4. Levy and Danford: unpublished (refer: Molten Salt Chem., ed. Blander, Interscience (1964)
5. Levy, Agron, Bredig and Danford: Ann. N.Y. Acad. Sci. 79 762 (1960)
6. Furukawa: Discuss Faraday Soc., 32 53 (1961)

i.e., there is a reduction of co-ordination number on melting. The most frequent nearest neighbour distance is shorter than in the solid by 0.04-0.27 Å.

Similar approaches have been made with alkali carbonates[1], sulphates[1], nitrates[2] and nitrites[2]. The first peak in the carbonate system, occuring at 1.3 Å, corresponds to the shortest interatomic distance C-O, of the $CO_3^{2-}$ ion. Estimation of the corresponding co-ordination number gives values from 2.6-3.2, suggesting that the carbonate ion is stable in fused alkali carbonates. In a like manner, the existence of the entities $SO_4^{2-}$[1], $NO_3^-$[3] and $NO_2^-$[3], has been substantiated.

To study the statistical distributions of the cations around polyatomic species, a model is required and predictions on the basis of the model compared to the experimental radial distribution curves. However, the estimation of areas subtended by peaks of the radial distribution curves is insufficiently precise to lead to definite conclusions. Indications are however, from the work of Zarzycki[1] on carbonates and sulphates, that as the cation is changed from lithium to potassium, there is an increased tendency for the cation to occupy sites nearer to the "corners" of the anions and to neglect the sites closer to their faces. This has the effect of allowing the anions greater rotational freedom.

---

1. Zarzycki: Discuss. Faraday Soc., 32 38 (1961)
2. Furukawa: Discuss. Faraday Soc., 32 53 (1961)
3. Furukawa: Sci. Reports Res. Inst. Tohoku Univ., A12 151 (1960)

Because of the difficulties and inherent inaccuracies in both x-ray and neutron diffraction measurements, systems of greater complexity than pure simple salts have not been examined.

b) Absorption spectra

Despite the lack of detail from the absorption spectra of pure salts, a comparison of the spectra of, for example, the molten alkali halides, with those of the corresponding crystals and gases, gives useful indications of structure. The substitution of Cs for Li, gives a slight shift of the absorption edge to the red end of the spectrum, while substitution of Br and I for Cl, produces a far more pronounced shift. One explanation of this phenomenon[1] is that an electron is transferred from the anion to a group of closely surrounding cations. This electronic state is pictured with the electron distribution over the walls of the cavity, composed of cations, in which the anion fits. The broad absorption bands characteristic of these salts are explained by the polarization effect caused by the penetration of the anion by the surrounding cations.

The absorption spectra of some salts are very different from the corresponding crystal spectra (e.g. AgCl(s) at 25°C has an absorption maximum at 254 mμ, while AgCl(l) at 475°C has a maximum at 535 mμ[1]). Such shifts are often interpreted in terms of complex ion formation. Sakai[2] found that the ultra-violet absorption spectra

---

1. Sundheim and Greenberg: J. Chem. Phys., 28 439 (1958)
2. Sakai: Bull. Chem. Soc. Japan, 31 500 (1958)

of aqueous solutions containing two salts, showed a shift towards a larger wavelength when the components formed a complex. In the molten system $NaCl-CdCl_2$, by comparison with the spectra obtained from the aqueous solution, Sakai postulated the existence of the complex ion $CdCl_4^{2-}$.

It has been possible to classify many spectra of molten transition metal salt solutions as octahedral-like or tetrahedral-like[1]. In cases where this does not hold, it is proposed that the deviations represent ligand configurations, that can be reasonably described as small distortions from simple cubic geometry[2,3].

c) Vibrational spectra

Knowledge of the chemical bonding and stereo-chemistry in inorganic melts can be advanced through the theory of molecular vibrations[4]. It is often possible[5] to distinguish the arrangement of atoms in a polyatomic species from the number of vibrational bands observed in its infra-red and Raman spectra, by reference to the total number of symmetry elements present in the species.

In spectra of gases, the line shape (and intensity) has been semiquantitatively analysed in terms of environmental interactions[5].

---

1. Smith: Molten Salt Chemistry, ed. Blander, Interscience Pub.,(1964)
2. Sundheim: The co-ordination of metal ion in Fused Salts, Proc. Intern. Conf. Co-ordination Chem., (1962)
3. Gruen and McBeth: J. Phys. Chem., 63 393 (1959)
4. Bellamy: The I.R. Spectra of Polyatomic Molecules, Wiley & Sons Inc. N.Y., (1954)
5. Breene Jr.: Rev. Mod. Phys., 29 94 (1957)

Similar analysis of liquid systems has been precluded by the complex nature of the interactions and the lack of a satisfactory distribution function[1]. Qualitative information has however been obtained by a comparison of the intensity of a vibration of given frequency with those for different salts[2].

Most vibrational spectral information has been derived for single salts[3]. The studies on molten two-component systems have been confined mainly to: (a) two ionic component systems, and (b) two component systems containing an ionic solute in a co-valent inorganic solvent (e.g. $HgCl_2$-KCl[3b]). With reference to group (a) the pyramidal $CdCl_3^-$ ion is evidently the predominant species in cadmium$^{II}$ halide - alkali metal halide melts, with tetrahedral $CdCl_4^{2-}$ present in lower concentrations[3a,4]. Similarly $PbCl_3^-$ (pyramidal) has been found to be the predominant species in $2PbCl_2.KCl$ and $PbCl_2.KCl$ melts, from Raman spectral evidence[5].

---


1. James: Molten Salt Chemistry, ed. Blander, Interscience Pub., (1964)
2. Wilmshurst: J. Chem. Phys., 36 2415 (1962)
3. See for example:
   chlorides (a) Bues: Z. anorg. u allgem. Chem., 279 104 (1955)
   (b) Janz and James: J. Chem. Phys., 38 902 (1963)
   nitrates (c) Janz and James: J. Chem. Phys., 35 739 (1961)
   chlorates (d) Wilmshurst: J. Chem. Phys., 36 2415 (1962)
4. Bredig and Van Artsdalen: J. Chem. Phys., 24 478 (1956)
5. Balasubrahmanyam and Nanis: J. Chem. Phys., 40 2657 (1964)

d) Nuclear Magnetic Resonance

Recently, nuclear magnetic resonance studies have been applied to molten thallium salts[1,2]. Although cations and anions are partly associated in the melts, the N.M.R. shifts of the thallium nucleus appear to be due to the co-valent bond linkage, rather than to polarization of the cation by the halide ions. This method of investigation is still in its infancy and little structural information is as yet available.

e) Conductance

As molten salts have specific conductance 20-100 times greater than that of aqueous electrolytes, conventional techniques of measurement cannot be employed[3,4]. The conductance of pure fused salts has been used to study the extent of dissociation and the nature of the conduction process. Thus, in the case of lithium chloride at its melting point (equivalent conductance = 183 mho $cm.^2$ $equiv.^{-1}$) and aluminium chloride at its melting point (equivalent conductance = $1.5 \times 10^{-5}$ mho $cm.^2$ $equiv.^{-1}$), the conclusion is drawn that LiCl is ionic and $AlCl_3$ is co-valent: $ZnCl_2$ (equivalent conductance = 0.02 mho $cm.^2$ $equiv.^{-1}$ at its m.pt.), is regarded as intermediate between the two. From the conductance of mixtures, information concerning the

---

1. Rowland and Bromberg: J. Chem. Phys., 29 626 (1958)
2. Hafner and Nachtrieb: J. Chem. Phys., 40 2891 (1964)
3. Reddy: J. Electrochem. Technol., 1 325 (1963)
4. Bloom and Bockris: Mod. Aspects of Electrochem. No.2, ed. Bockris, Butterworth Sci. Pubs., (1959)

structure of molten salts has been obtained, as well as evidence for complex ion formation in many systems.

The equivalent conductance of an electrolyte is given by:

$$\Lambda = kV_E = kE/\rho \qquad (1.6)$$

where k is the specific conductance, $V_E$ the equivalent volume, $\rho$ the density and E the equivalent weight.

For mixed electrolytes:

$$\Lambda = k\bar{E}/\rho \qquad (1.7)$$

where $\bar{E}$ = mean equivalent weight

$$= f_1E_1 + f_2E_2 \qquad (1.8)$$

where $f_1$ is the equivalent fraction and $E_1$ the equivalent weight of component 1, etc.

The linearity of the plot of log k or log $\Lambda$ vs. 1/T, has been explained by analogy to the conductance of solid salts[1]. For a simple salt consisting of cations and anions, the specific conductance is given by[2]:

$$k = A_1e^{-E_1/RT} + A_2e^{-E_2/RT} \qquad (1.9)$$

where $E_1$ and $E_2$ are the activation energies for ionic migration of cation and anion respectively and $A_1$ and $A_2$ are constants. This equation assumes that no constitutional change takes place with increasing temperature. If $E_1$ and $E_2$ are either nearly equal or very different, then eqn. (1.9) reduces to the simple Arrhenius relationship:

$$k = A'e^{-E_k/RT} \qquad (1.10)$$

---

1. Frenkel: The Kinetic Theory of Liquids, Oxford, (1946)
2. Eucken: Die Chemie, 55 163 (1942)

where $E_k$ is the activation energy for ionic migration of the molten electrolyte. When $E_k$ is not equal to $E_\Lambda$ , then:

$$\Lambda = Ae^{-E_\Lambda/RT} \qquad (1.11)$$

Plots of $\log\Lambda$ vs. $1/T$ for pure fused alkali halides (except LiCl) are slightly curved[1,2]. This has been explained qualitatively in terms of opposing factors, involving changes in coulombic interaction and numbers of nearest neighbours with change of temperature.

For mixtures of molten salts:

$$\Lambda = Ae^{-E_\Lambda/RT} + A'e^{-E'_\Lambda/RT} \qquad (1.12)$$

where A, A' are constants. Experimentally[3], $\log\Lambda$ is a linear function of $1/T$ and therefore $E_\Lambda$ is either approximately equal to or much greater than $E'_\Lambda$ .

Bockris et al.[4] have derived an equation for the temperature dependence of $\Lambda$ using the transition state theory of reaction rates:

$$\Lambda_i = 5.18 \times 10^{-18} (\varepsilon + 2) d_i^2 \exp.(\Delta S_i^{\neq}/R) \exp.(-\Delta H_i^{\neq}/RT) \qquad (1.13)$$

where $d_i$ = half migration distance for the conducting ion

" $\varepsilon$ = dielectric constant of the medium

" $\Delta S_i^{\neq}$ = entropy of activation for ionic migration

" $\Delta H_i^{\neq}$ = energy of activation (= E in eqn. 1.11)

---


1. Van Artsdalen and Yaffe: J. Phys. Chem., 59 118 (1955)
2. Yaffe and Van Artsdalen: ibid., 60 1125 (1956)
3. Bloom and Heymann: Proc. Roy. Soc., A188 392 (1947)
4. Bockris, Kitchener, Ignatowicz and Tomlinson: Trans. Faraday Soc., 48 75 (1952)

Although values have been chosen for $\varepsilon$ [1-3], the inherent uncertainties make estimation of $\Lambda_i$ difficult.

Conductance investigations[3-8] have indicated that the activation energy for ionic migration can suggest changes in the constitution of mixtures of molten salts. A maximum in the activation energy in relation to composition has been interpreted as a change in the size of the conducting species, or a change in the interionic force fields.

f) Diffusion

The self diffusion coefficients of individual ionic species in molten salts has been measured by means of radioactive and stable isotopes as tracers*. The self diffusion coefficient, D, of a species, may be expressed by an Arrhenius rate equation, i.e.,

$$D = A \exp. (-\Delta H_D^{\neq}/RT) \qquad (1.14)$$

---

* Most tracer work in diffusion has been done using radioactive isotopes. However stable isotopes have been used by Lunden, e.g.,
Lunden: Z. Naturforsch, 14a 801 (1959); 15a 1019 (1960)
Ann. N.Y. Acad. Sci., 79 988 (1960)
Trans. Chalmers Univ. Technol., Gothenburg, 241 (1961)


1. Van Artsdalen and Yaffe: J. Phys. Chem., 59 118 (1955)
2. Yaffe and Van Artsdalen: ibid., 60 1125 (1956)
3. Bockris, Kitchener and Davis: Trans. Faraday Soc., 48 536 (1952)
4. Karpachev, Stromberg and Pôltoratskaya: J. Phys. Chem., (U.S.S.R.) 5 793 (1934)
5. Harrap and Heymann: Trans. Faraday Soc., 51 259, 268 (1955)
6. Bockris, Kitchener, Ignatowitz and Tomlinson: Trans. Faraday Soc., 48 75 (1952)
7. Bockris, Kitchener, Ignatowitz and Tomlinson: Discuss. Faraday Soc., 4 265 (1948)
8. Bloom and Heymann: Proc. Roy. Soc., A188 392 (1947)

where A is a constant, $\Delta H_D^{\neq}$, is the energy of activation for diffusion, R is the gas constant and T is the absolute temperature. The diffusion coefficient is related to the equivalent ionic conductance by the Nernst-Einstein equation, viz:

$$\Lambda_i = Z_i F^2/RT.D_i \qquad (1.15)$$

where $D_i$, $\Lambda_i$ are the diffusion coefficient and equivalent ionic conductance of an ion i, with valency $Z_i$. The Nernst-Einstein relationship has been found inapplicable to molten salts and the following explanations have been suggested:

(i) Mutual friction of the moving ions would result in such inapplicability, even if ionic movements were common to both diffusion and conduction[1-3].

(ii) A correction factor[4] is applied to the calculation of ionic crystal conductance from measurements of self diffusion coefficients in the crystal, on the basis of non-random "tracer" jumps in the lattice. This phenomenon has been applied to ionic liquids by Bockris and Hooper[5].

(iii) By means of paired vacancy diffusion[6,7] simultaneous movement of cation and anion is assumed; such a mode of ionic migration should contribute to diffusion but not to conductance[5].

---


1. Laity: Ann. N.Y. Acad. Sci., 79 997 (1960)
2. Laity: J. Chem. Phys., 30 682 (1959)
3. Klemm: Z. Naturforsch, 8a 397 (1953); 15a 173 (1960)
4. Bardeen and Herring: Imperfections in nearly perfect crystals; Wiley & Sons, Inc., N.Y. (1952)
5. Bockris and Hooper: Discuss. Faraday Soc., 32 218 (1961)
6. Seitz: Rev. Mod. Phys., 18 384 (1946)
7. Dienes: J. Chem. Phys., 16 620 (1948)

Potentially the determination of diffusion coefficients may provide considerable information concerning the structure of a liquid. Unfortunately however, no method has been developed that will yield reliable and accurate experimental data. Essential to such measurements are the establishment of a sharp planar boundary at the commencement of diffusion, the prevention of transport by convection and the termination of the diffusion process without altering the distribution of radiotracer about the boundary.[1]

Bockris and Angell[2] have studied the rate of self diffusion of cadmium ions in mixtures of $CdCl_2$ and KCl. Although contrary to the results of Raman spectra and electrical conductance studies[3], their results suggested the presence of the species $CdCl_3^-$. Self diffusion in molten $PbCl_2$ has been investigated by Perkins et al.[4,5] and the Arrhenius equation (1.14) shown to be valid for both ions; the activation energies for diffusion were found to be nearly identical. The same workers, in investigating the system $PbCl_2$-KCl, suggested $Pb_2Cl_5^-$ as a complex species present in the melt[6].

---


1. Easteal: M.Sc. thesis, University of New Zealand, (1961)
2. Bockris and Angell: Electrochim. Acta, 1 308 (1959)
3. Bredig: ibid., 5 299 (1961)
4. Perkins Jr., Escue, Lamb and Tidwell: J. Phys. Chem., 64 495 (1960)
5. Perkins Jr., Escue, Lamb and Wimberley: ibid., 64 1792 (1960)
6. Perkins Jr., Escue, Lamb, Tidwell and Wimberley: ibid., 64 1911 (1960)

g) Transport Numbers

The concept of transport numbers in pure fused electrolytes is either meaningful or not, depending on the frame of reference chosen[1]. Cation and anion transport numbers have no significance when defined with reference to the electrodes of the system[2], for in this case the passage of one faraday of electricity discharges are equivalent of cations and anions at the cathode and anode respectively. Thus either $t_+ = 1$ and $t_- = 0$, or $t_+ = 0$ and $t_- = 1$. Transport numbers in aqueous solutions are defined with reference to the "stationary" solvent. Such a situation does not exist in a pure salt and therefore the transport number cannot be defined. The problem is overcome by dividing the transport cell into two compartments by a porous disc. Provided bulk flow does not occur, the ionic transport numbers can be measured with respect to the disc as reference[1,3,4].

A considerable discrepancy in the experimental results for the transport numbers of molten salts is apparent in the literature and the theoretical interpretation which can be derived from this method of investigation is therefore questionable. For pure lead chloride for example, there are two sets of data: Duke and Laity[4]

---

1. Bloom and Easteal: Proc. First Australian Conf. Electrochem., ed. Friend and Gutmann, Pergamon (1965)

2. Swarz: Z. Elektrochem., 45 740 (1939)

3. Bloom and Doull: J. Phys. Chem., 60 620 (1956)

4. Duke and Laity: J. Am. Chem. Soc., 76 4046 (1954)
J. Phys. Chem., 59 549 (1955)

($t_- = 0.758$), Karpachev and Pal'guev[1] ($t_- = 0.8$), Delimarskii, Turov and Gitman[2] ($t_-^\circ = 0.83$), as opposed to Bloom and Doull[3] ($t_- = 0.379$) and Bloom and Easteal[4] ($t_- = 0.37$).

Experiments involving binary mixtures are regarded[5,6] as giving more comprehensive results, because in such systems a common ion serves as a frame of reference against which to measure the relative mobilities of the other species.

Aziz and Wetmore[7] defined the transport fractions $\mathcal{O}_i$, as the number of equivalents of the $i^{th}$ ion transported per faraday of charge passing through the melt. Using expressions for material balance, they derived the equation:

$$\Phi = 1 - \mathcal{O}_1 - N_1^\circ \mathcal{O}_3 = n_1 + n_2 (N_1 - N_1^\circ)/Z \qquad (1.16)$$

where $N_1^\circ$ is the initial and $N_1$ the final mole fraction of component 1, after the passage of Z faradays of charge, $n_1$ and $n_2$ are the number of equivalents of species 1 and 2 in the anolyte after electrolysis, while the subscript 3 represents the common ion. The experimental results did not allow the computation of $\mathcal{O}_2$.

---


1. Karpachev and Pal'guev: Zhur. Fiz. Khim., 23 942 (1949)
2. Belimarskii, Turov and Gitman: Ukrain. Khim. Zhur., 21 314 (1955)
3. Bloom and Doull: J. Phys. Chem., 60 620 (1956)
4. Bloom and Easteal: Proc. First Australian Conf. Electrochem., ed. Friend & Gutmann, Pergamon (1965)
5. Bloom and Bockris: Mod. Aspects of Electrochem., No.2, ed. Bockris, Butterworth Sci. Pubs., (1959)
6. Reddy: J. Electrochem. Technol., 1 325 (1963)
7. Aziz and Wetmore: Can. J. Chem., 30 779 (1952)

Duke et al.[1], however, showed that changes in concentration and volumes combined, gave sufficient information to calculate all the transport fractions. In the system $AgNO_3$-$NaNO_3$, $\sigma_3$, for the nitrate ion was found to be constant over the whole range of composition, while $\sigma_1$ and $\sigma_2$ were linear with respect to mole fraction. From this it was concluded that the system $Ag/Na/NO_3$ was completely dissociated.

Duke and Fleming[2] have studied transference in the system $PbCl_2$-KCl, using radioactive chlorine to obtain the transference fraction of chloride ions. From evaluation of the $\Phi$ function, they concluded that $Pb^{2+}$ exists in equilibrium with $PbCl^+$.

h) Viscosity

The viscosity $\eta$, of molten salts is generally represented by the equation:

$$\eta = A \exp. (E_{VIS.}/RT) \qquad (1.17)$$

where A is a constant for a particular liquid and $E_{VIS.}$ is the activation energy for viscous flow. Such equations have been suggested by a number of workers[3-5]. According to eqn. (1.17), the plot of log $\eta$ vs. 1/T is linear (this has been verified for a number

---

1. Duke, Laity and Owens: J. Electrochem. Soc., 104 299 (1957)
2. Duke and Fleming: J. Electrochem. Soc., 106 130 (1959)
3. Andrade: Phil. Mag., 17 698 (1934)
4. Dunn: Trans. Faraday Soc., 22 401 (1926)
5. de Guzman: Anal. Fis. Quim., 9 353 (1913)

of fused salts[1-3]) and from the gradient the activation energy for viscous flow can be obtained. $E_{VIS.}$ is always greater than $E_{\Lambda}$, indicating that a much greater configurational change is involved in viscous flow than in ionic migration[4]. Whereas conductance is determined by the transport of current due to the smaller ion, viscosity, measured in a field free environment, is determined mainly by the shearing forces between larger ions or groups. Viscosity measurements can therefore give information regarding the nature of the entities present in the melt.

In the systems $PbCl_2$-KCl and $CdCl_2$-KCl[5] no maxima are present in the plots of (a), viscosity vs. composition and (b) $E_{VIS.}$ vs. composition, suggesting the absence of large associated species. This conclusion however is contrary to the evidence obtained from conductance and density measurements. Harrap and Heymann explain the absence of maxima as follows:

> The free volumes in these systems display positive deviations from additivity. It is therefore considered[5] that the "enlarged size of some of the flow units in the system as a result of complex ion formation, would be offset to a large extent by the increase in free volume of the liquid: consequently the viscosity isotherm would not necessarily be expected to show positive deviations from additivity". This has

---

1. Bockris and Lowe: Proc. Roy. Soc., 226A 423 (1954)
2. Bloom, Harrap and Heymann: Proc. Roy. Soc., 194A 237 (1948)
3. Harrap and Heymann: Trans. Faraday Soc., 51 259 (1955)
4. Bloom and Heymann: Proc. Roy. Soc., 188A 392 (1947)
5. Harrap and Heymann: Trans. Faraday Soc., 51 259, 268 (1955)

the effect of decreasing the energy of activation[1]. This example demonstrates the care that must be taken in deducing the nature of the structural species present in the liquid.

According to Mackenzie[2] viscous flow is a passage from one equilibrium position to another in the direction of the applied stress, a movement requiring the presence of holes in the liquid. The total activation energy is regarded as being made up of:

(1) energy required to establish a suitable configuration, and

(2) energy required for the moving species to move into a new arrangement.

1) Density and Molar Volume

Density measurements on single and mixed pure salts in the solid and liquid state, yield information concerning the volume increase accompanying melting. Values at different temperatures suggest changes in the structural groups present in the melt. The density $\rho$, of molten salts varies linearly with temperature and is normally expressed in the form:

$$\rho = a - bt, \qquad (1.18)$$

where a and b are constants. Molar volumes Vm, are calculated from densities by the equation:

$$Vm = M/\rho \quad , \qquad (1.19)$$

where M is the molecular weight of the salt.

---

1. Richards: Ph.D. thesis, University of New Zealand, (1956)
2. Mackenzie: J. Chem. Phys., 28 1037 (1958)

For mixtures:

$$Vm = \bar{M}/\rho \quad , \tag{1.20}$$

where

$$\bar{M} = M_1N_1 + M_2N_2 \tag{1.21}$$

( = mean molecular weight)

and where $M_1$ and $N_1$ are the molecular weight and mole fraction of component 1, etc. Generally a linear relationship between molar volume and mole fraction is regarded as representing ideal behaviour[1].

Density measurements are rather insensitive to interactions within the melt and therefore quantitative information about such cannot be deduced. It is worth noting however, that the system $NaNO_3$-$NaNO_2$ exhibits "ideal" behaviour, whereas other systems such as $CdCl_2$-KCl, $PbCl_2$-KCl, $CdI_2$-KI, show positive and $PbCl_2$-$CdCl_2$, $BaCl_2$-$CdCl_2$, show negative deviations from the ideal value[2,3].

It has been suggested[4] that in systems containing polarizing and polarizable ions, a change in bond type can occur, depending on the nature of the ions in the melt. Klemm[5] proposed that melts consisting of co-valent molecules (implying a certain degree of co-valent bonding between interacting species) would have larger molar volumes than purely ionic melts where the interionic forces would be stronger. Hence an inference can be drawn[4], for example, in the system $CdCl_2$-KCl,

---

1. See for example:
   (a) Bloom and Heymann: Proc. Roy. Soc., 188A 392 (1947)
   (b) Van Artsdalen and Yaffe: J. Phys. Chem., 59 118 (1955)
   (c) Boardman, Dorman and Heymann: J. Phys. Chem., 53 375 (1949)
2. Bloom, Knaggs, Molloy and Welch: Trans. Faraday Soc., 49 1458 (1953)
3. Bloom and Bockris: Mod. Aspects of Electrochem,, No.2, ed. Bockris Butterworth Sci. Pubs., (1959)
4. Richards: Ph.D. thesis, University of New Zealand (1956)
5. Klemm: Z. anorg. u allgem. Chem., 152 235 (1926)

where marked positive deviations from the ideal are observed[1], as to the more co-valent nature of the melt compared to the two pure components.

j) Compressibility

The isothermal compressibility of a substance can be derived from pressure-volume relationships when the substance is contained in a pressure vessel[2]. The compressibilities have also been measured at high pressures, using shock waves[3]. Bockris and others[4-6] have measured ultrasonic velocities of some molten salts at high temperatures, where the adiabatic compressibility ($\beta_s$), is given by:

$$\beta_s = 1/\rho u^2 \qquad (1.22)$$

where $\rho$, is the density and u the velocity of sound in the system. The isothermal compressibility ($\beta_T$), is calculated from knowledge of the ratio $\gamma$ ($= C_p/C_v$), by means of the equation:

$$\beta_T = \gamma/u^2\rho = \beta_s\gamma \qquad (1.23)$$

where $C_p$ and $C_v$ are the heat capacity at constant pressure and constant volume respectively. Values of the compressibilities for various melts have been used by Bockris and Richards[5] to obtain an equation of state for molten salts.

---


1. Boardman, Dorman and Heymann: J. Phys. Chem., 53 375 (1949)
2. Bridgman: "Physics of High Pressure", Bell & Sons Ltd., (London) (1951)
3. Rice, McQueen and Walsh: "Solid State Physics", Read Press Inc., N.Y., (1958)
4. Bloom and Bockris: J. Phys. Chem., 61 515 (1957)
5. Bockris and Richards: Proc. Roy. Soc., 241 44 (1957)
6. Richards, Brauner and Bockris: British J. Appl. Phys., 6 387 (1955)

k) Surface Tension

Surface tension values for molten salts are usually obtained using the method of maximum bubble pressure[1]. Generally, surface tension $\gamma$, varies with temperature according to the linear relationship:

$$\gamma = a-bt \qquad (1.24)$$

Where a and b are empirical constants. When relationships for surface tensions of ordinary room temperature liquids are applied to molten salts, marked inconsistencies are found.

For example:

(i) The Eötvös relationship[2]:

$$\gamma V_m^{2/3} = K(t_c-6-t) \qquad (1.25)$$

where Vm is the molar volume, K the Eötvos constant and $t_c$ the critical temperature, has been found to give anomalous values for K.

(ii) Sugden's parachor (P)[3], expressed by:

$$P = \frac{M\gamma^{\frac{1}{4}}}{\rho - d} \qquad (1.26)$$

where $\rho$, is the density of the liquid and d the density of the vapour, is temperature dependent for molten salts[4-6].

---


1. See for example: Boardman, Palmer and Heymann: Trans. Faraday Soc., 51 277 (1955)
2. Bloom: Rev. Pure and Appl. Chem., 9 139 (1959)
3. Sugden: "The Parachor and Valency", Reutledge (London, 1930)
4. Bloom, Davis and James: Trans. Faraday Soc., 56 1179 (1960)
5. Peake and Bothwell: J. Am. Chem. Soc., 76 2653 (1954)
6. Boardman, Palmer and Heymann: Trans. Faraday Soc., 51 277 (1955)

The thermodynamic treatment of Guggenheim[1] for the surface tension of mixtures, has been applied to ionic liquids[2,3]. Certain systems, e.g., $NaNO_3$-$KNO_3$, have been shown[2] to give surface tension isotherms very close to the ideal values. Binary systems of $PbCl_2$ with the alkali chlorides on the other hand give deviations of surface tensions from ideality which increase with increasing alkali cation radius[3].

The surface heat of mixing has been used[4] in discussion of interactions in molten salt mixtures, since the formation of complex ions would be expected to contribute to a decrease of the surface heat of mixing, as well as to a decrease of heat content on mixing in the bulk phase[5]. The surface heat of mixing per unit area ($\Delta H^s/a$), is defined as:

$$\Delta H^s/a = \frac{H^s}{a} - \left[ N_1 \frac{(H^s)}{(a)_1} + N_2 \frac{(H^s)}{(a)_2} \right] \qquad (1.27)$$

$$= 0 \text{ if the system is ideal,}$$

where $H^s/a$ ($= \gamma - T\frac{d\gamma}{dT}$), is the value for the mixture and $(H^s/a)_1$ is the value for the component whose mole fraction is $N_1$, etc. For the system $PbCl_2$-RbCl, a minimum in the graph of $H^s/a$ against composition is found and this may be interpreted in terms of complex formation.

---


1. Guggenheim: "Mixtures", Oxford Univ. Press, N.Y. (1952)
2. Boardman, Palmer and Heymann: Trans. Faraday Soc., 51 277 (1955)
3. Dahl and Duke: U.S. Atomic Energy Comm., ISC-923 (1958)
4. Bloom, Davis and James: Trans. Faraday Soc., 56 1179 (1960)
5. Bloom and Bockris: "Fused Salts", ed. Sundheim, McGraw Hill Book Co. (1964)

Surface tension measurements have been further used to calculate the energy $E_h$, required to form holes in molten salts[1], on the basis of the equation:

$$E_h = 4 \pi r_h^2 \gamma \qquad (1.28)$$

where $r_h$ is the mean hole radius.

1) Refractive Index and Molar Refractivity

This method of investigation has received very little attention. The refractive index is found to have an inverse linear dependence on temperature for molten salts. Molar refractivity R is calculated using the Lorentz-Lorenz equation[2,3]:

$$R = \frac{n^2-1}{n^2+2} \frac{M}{\rho} \qquad (1.29)$$

where M and $\rho$ are the molecular weight and density respectively. For most molten salts, the molar refractivity is independent of temperature over small temperature ranges. For mixtures $\bar{M}$ the mean molecular weight (see eqn. 1.21) is substituted for M[4,5].

In simple molten salt binary systems, molar refractivity is an additive property[6]. Positive deviations from additivity have been observed in such systems as $CdCl_2$-KCl and $PbCl_2$-KCl[7].

---


1. Bockris and Richards: Proc. Roy. Soc., 241 44 (1957)
2. Lorenz: Ann. Physik, 11 70 (1880)
3. Lorentz: Ann. Physik, 9 641 (1880)
4. Thurmond: J. Am. Chem. Soc., 75 3928 (1953)
5. Bloom and Rhodes: J. Phys. Chem., 60 791 (1956)
6. Bloom and Bockris: Mod. Aspects of Electrochem., No.2, ed. Bockris, Butterworth Sci. Pubs. (1959)
7. Bloom and Peryer: Aust. J. Chem., (1965)

m) Thermal Properties

Measurements of heat capacity, thermal conductivity and heat and entropy of fusion, have received little attention. This work is summarized by Kelley[1], Gambill[2] and Bloom et al.[3]

n) Thermodynamic Properties

The following will be discussed in section 1.6:

(i) Equilibrium distribution of a solute between two immiscible solvents.

(ii) Vapour pressure determinations.

(iii) Electromotive force measurements.

o) Polarography and Voltammetry

The term polarography refers to the measurement of current-voltage curves with a dropping mercury electrode, while voltammetry is used to indicate the same measurement utilising a solid micro-electrode. Since electron transfer reactions are fast in fused salts, mass transfer often is the rate controlling step in an electrode process and under these conditions, such techniques give information concerning electrode reactions. Current-potential curves frequently furnish information pertaining to the reversibility of an electrode system and often elucidate reduction steps, the number of electrons involved and the prevalence of diffusive conditions in electrode processes. Polarography and voltammetry have also been used to study complex formation, electrode kinetics and mass transport in molten salts.

1. Kelley: U.S. Bur. Mines Bull., 393 (1936)
2. Gambill: Chem. Engineering, 66 No.25 169 (1959)
3. Bloom and Doroszkowski: Aust. J. Sci., (1965)

The use of the dropping mercury electrode has been extended from room temperature liquids to low melting systems by Nachtrieb and Steinberg[1,2], who studied the reduction waves of a number of molten ions in molten $LiNO_3$ - $NH_4NO_3$ - $NH_4Cl$ and $LiNO_3$ - $NaNO_3$ - $KNO_3$ at 160°C. Apart from dropping mercury electrodes, which have been used by several workers[3-5], the only other metal which has been successfully tested has been bismuth[6]. However, technical difficulties, resulting from preparation and chemical attack, prevent this electrode from being used generally.

For higher operating temperatures, solid electrode voltammetric techniques are used but these introduce such problems as the accurate measurement of the electrode surface area[7]. Difficulty is also encountered in the establishment of reproducible reference electrodes, where the nature of the solvent and the high operating temperatures, cause complications not encountered in aqueous solutions. Reference electrodes commonly used are: gas electrodes (e.g. chlorine[8], oxygen[9]), metal ion - metal

---


1. Nachtrieb and Steinberg: J. Am. Chem. Soc., 70 2613 (1948)
2. Steinberg and Nachtrieb: ibid., 72 3558 (1950)
3. Randles and White: Z. Elektrochem., 59 666 (1955)
4. Christie and Osteryoung: J. Am. Chem. Soc., 82 1841 (1960)
5. Egan: J. Phys. Chem., 65 2222 (1961)
6. Heus and Egan: J. Electrochem. Soc., 107 824 (1960)
7. Liu, Johnson and Laitinen: Molten Salt Chem., ed. Blander, Interscience (1964)
8. Wachter and Hildebrand: J. Am. Chem. Soc., 52 4655 (1930)
9. Karpachev and Poltoratskaya: Zh. Fiz. Khim., 9 145 (1931)

electrode[1-3], noble metal electrode[4] and glass membrane electrode[5].

Although experimental difficulty in molten salts and the lack of information on the solvent systems have not enabled precise knowledge of the electrode processes, the use of voltammetry has provided a convenient means of investigation in the field of electrode reactions.

p) Chronopotentiometry

Chronopotentiometry involves the measurement of the time interval between the onset of constant current electrolysis in an unstirred solution and the point at which a state of complete concentration polarization is attained. The interval is referred to as the transition time and is a function of the concentration of the substance electrolysed.

Laitinen and Ferguson[6] have demonstrated the applicability of chronopotentiometry to fused salts (in LiCl-KCl eutectic) using a platinum microelectrode. They found that metallic impurities in the melt resulted in a residual transition time. Similar measurements have been conducted by Van Norman[7] for liquid bismuth pool electrodes in contact with a fused LiCl-KCl eutectic, to study the oxidation of

---

1. Laitinen, Liu and Ferguson: Anal. Chem., 30 1266 (1958)
2. Liu: J. Phys. Chem., 66 164 (1962)
3. Fiontelli and Montanelli: J. Chem. Phys., 22 1781 (1954)
4. Delimarskii, Panchenko and Shilina: Collect. Czech. Chem. Commun., 25 3061 (1960)
5. Delimarskii: Zapiski Inst. Khim., Akad. Nauk. Ukr., R.S.R., 8 23 (1946)
6. Laitinen and Ferguson: Anal. Chem., 29 4 (1957)
7. Van Norman: Anal. Chem., 33 946 (1961)

lithium and zinc dissolved in the bismuth. Diffusion coefficients for these metals in bismuth were calculated and evidence for an intermolecular compound between Bi and Li was found. Inman and Bockris[1] have used chronopotentiometry in the liquid mixture $KNO_3$-$NaNO_3$ (equimolar) to study complex formation constants (using the method of Deford and Hume[2]) for various complexes.

Chronopotentiometry has proved to date to be one of the most accurate and important analytical methods in fused salts, with a reported accuracy of 2-4%.

---

1. Inman and Bockris: Trans. Faraday Soc., 57 2308 (1961)
2. Deford and Hume: J. Am. Chem. Soc., 73 5321 (1951)

## 1.5 THE CONCEPT OF THERMODYNAMIC ACTIVITY IN MOLTEN SALTS

### a) General

The activity of component A in a mixture is defined by:

$$\mu_A - \mu_A^\circ = RT \ln a_A \qquad (1.30)$$

where $\mu_A^\circ$ is the chemical potential of A in its pure state and $\mu_A$ is the chemical potential in the mixture. The activity may also be expressed as the relative fugacity, which at low pressures, approximates the relative vapour pressure, i.e.,

$$a_A = f_A/f_A^\circ \approx P_A/P_A^\circ \qquad (1.31)$$

where $f_A$ and $P_A$ are the fugacities and partial pressures of A above the mixture and $f_A^\circ$ and $P_A^\circ$ refer to the standard state at the same temperature. Thus in the standard state the activity $a^\circ = 1$.

For molten salts the standard state is chosen as the pure liquid, i.e., the standard state of component A is that mixture for which the mole fraction of A is unity. In thermodynamic considerations it is important that no matter what changes component A may undergo on mixing with B, e.g., complexing, dissociation, etc., the value of $a_A$ obtained will always reflect changes in degree of ionization or structure of the solvent with reference to the standard state.

b) The relationship between activity and composition in molten salt mixtures

By analogy with aqueous solutions, where the activity of a salt is expressed by its ionic activity product, Temkin[1] assumed complete ionization and derived the expression:

$$a_{(M_1)_m(X_1)_n} = (N_{M_1})^m \cdot (N_{X_1})^n \qquad (1.32)$$

where $a_{(M_1)_m(X_1)_n}$ is the activity of the salt $(M_1)_m(X_1)_n$

" $(N_{M_1})$ is the cationic fraction of $M_1$

" $(N_{X_1})$ is the anionic fraction of $X_1$

Temkin defined the ionic fractions as:

$$\begin{aligned} N_{M_1} &= n_{M_1}/(n_{M_1} + n_{M_2} + \ldots\ldots n_{M_i}) \\ &= n_{M_1}/\sum n_{M_i} \\ N_{X_1} &= n_{X_1}/(n_{X_1} + n_{X_2} + \ldots\ldots n_{X_i}) \\ &= n_{X_1}/\sum n_{X_i} \end{aligned} \qquad (1.33)$$

where $n_{M_1}$ is the number of $M_1$ ions and $\sum n_{M_i}$ is the total number of cations, etc. Statistically this means that the cations $M_1$, $M_2$, etc., are randomly distributed over the cation positions of a quasi-lattice in the mixture regardless of the magnitude of their charge, and likewise for the anions.

Thus for a mixture of $M_1^+$ and $M_2^{2+}$, $N_{M_1}{}^+$ and $N_{M_2}{}^{2+}$ are given by:

$$\begin{aligned} N_{M_1}{}^+ &= n_{M_1}{}^+/(n_{M_1}{}^+ + n_{M_2}{}^{2+}) \\ N_{M_2}{}^{2+} &= n_{M_2}{}^{2+}/(n_{M_1}{}^+ + n_{M_2}{}^{2+}) \end{aligned} \qquad (1.34)$$

and an analagous expression holds for the anions.

---

1. Temkin: Acta. Physiochim. U.R.S.S., 20 411 (1945)

Flood et al.[1,2], with reference to mixed ionic crystals, regarded the isomorphous substitution of a monovalent ion by a divalent ion as requiring the formation of a vacant cation position according to the scheme ($M^{2+} + \square = 2M^{+}$).A divalent cation is therefore regarded as equivalent to an adjacent pair of monovalent cations. Hence the cation fractions become, (c.f. eqn. 1.34):

$$N_{M_2}{}^{2+} = n_{M_2}{}^{2+}/(n_{M_2}{}^{2+} + \tfrac{1}{2}n_{M_1}{}^{+})$$
$$N_{M_1}{}^{+} = \tfrac{1}{2}n_{M_1}{}^{+}/(n_{M_2}{}^{2+} + \tfrac{1}{2}n_{M_1}{}^{+}) \qquad (1.35)$$

The ionic fraction model proposed by Herasymenko[3], regards the cations and anions to be distributed in the melt regardless of the sign or magnitude of their charge.

Hence:

$$N_{M_1}{}^{+} = n_{M_1}{}^{+}/(\sum n_{M_1}{}^{+} + \sum n_{X_1}{}^{-}) \qquad (1.36)$$

This situation parallels that of an ionic gas. However, the temperatures required for the thermal motion to exceed the electrostatic binding energy between oppositely charged particles is so great, (e.g., 100,000°C for NaCl) that this model is impractical.

The implied degree of disorder increases in going from the solid solution model for the ionic fractions as proposed by Flood et al.[1,2], to the gas-like model of Herasymenko[3]. It may be supposed that the Temkin model gives the truest representation of the molten state, lying as it does somewhere between the extremes of the

---

1. Flood, Førland and Grjotheim: Inst. Min. Met. Symp., Molten Slags (1953)

2. Flood, Førland and Grjotheim: Z. anorg. u allgem. Chem., 276 289 (1954)

3. Herasymenko: Trans. Faraday Soc., 34 1245 (1938)

other two. This is not quite the case however: excluding the Herasymenko model for its impractability, the Temkin model generally gives the best agreement, especially for binary systems but that of Flood et al., is found to be more applicable for reciprocal systems[1].

For molten salts, the activity coefficient $\gamma$, is defined by the expression:

$$a_{M_1X_1} = a'_{M_1X_1} \cdot \gamma_{M_1X_1} \qquad (1.37)$$

where $a'_{M_1X_i}$ is the ideal Temkin activity calculated from eqn. 1.32. For binary systems, the ideal Temkin activity for component 1 is equivalent to the mole fraction of that component, i.e., $a'_{M_1X_1} = N_{M_1X_1}$. The ideal Temkin activity in a mixture of $M_1X_1$ and $M_2X_2$ may be explained qualitatively as follows. If the two cations and the two anions have the same physical properties, then the cations can mix randomly in the cation regions of position which are adjacent to the anions and vice versa for the anions. The total enthalpy and energy of the solution is the same as that of the pure components and the heat and energy of mixing are zero. The total entropy of mixing can be calculated from the total number of possible equivalent and distinguishable configurations.

Most molten salt systems exhibit non-ideal behaviour, in that they show either positive or negative deviations from the ideal Temkin activity. This can be interpreted in terms of interactions within the melt resulting in non-random mixing of the cations and also of the anions. Interaction effects which would influence the magnitude

---

1. See for example - Bloom and Welch: Trans. Faraday Soc., 57 61 (1961)

of the activity are as follows[1]:

1. Coulomb effects resulting in repulsion between next-nearest neighbours.
2. Polarization effects which would be present because of the different sizes and charges of ions of like sign. For example, an anion having as nearest neighbours two cations of similar size but different charge, will be polarized, owing to the resulting coulombic field intensity, in such a way that the negative charge on the anion will tend to accumulate near the cation of greatest charge density.
3. Van der Waal's interaction effects.
4. Ligand field effects which tend to stabilise the pure salts of transition metal ions and result in more probable configurations of near-neighbour anions.
5. Packing and steric effects. Highly charged cations will tend to have a larger number of anions as nearest neighbours, than cations of low charge. Energy changes related to this effect will depend on the anion-cation radius ratio.

---

1. Blander: Molten Salt Chemistry, ed. Blander, Interscience, (1964)

## 1.6 METHODS OF MEASURING ACTIVITIES IN MOLTEN SALTS

a) Vapour pressure measurements

The chemical potential $\mu_1$, of a component 1, in a mixture, is related to the fugacity $f_1$, of that component by:

$$\mu_1 = RT \ln f_1 \qquad (1.38)$$

For the pure liquid:

$$\mu^\circ = RT \ln f_1^\circ \qquad (1.39)$$

and hence (c.f. eqn. 1.30):

$$\mu_1 - \mu_1^\circ = RT \ln f_1/f_1^\circ = RT \ln a_1 \qquad (1.40)$$

It is assumed that except for the formation of associated species or compounds in the vapour, the vapour behaves ideally, so that the fugacity of a species in the vapour is equal to the partial pressure of the species[1], so that $f_1 = p_1$, etc.

Then from 1.40:

$$\mu_1 - \mu_1^\circ = RT \ln p_1/p_1^\circ = RT \ln a_1 \qquad (1.41)$$

If a monomeric molecule $M_1$, in the vapour, associates into dimers, trimers, etc., then:

$$M_1 \rightleftharpoons \tfrac{1}{2}(M_1)_2 \rightleftharpoons \tfrac{1}{3}(M_1)_3 \rightleftharpoons \tfrac{1}{i}(M_1)_i \qquad (1.42)$$

where $(M_1)_2$ represents the dimer, etc. Then the total pressure P, assuming the presence of only one component in the vapour (i.e. $M_1$, $(M_1)_2$, etc.) will be given by:

$$\begin{aligned} P &= (p_1)_1 + (p_1)_2 + \ldots\ldots (p_1)_i \\ &= \sum (p_1)_i \end{aligned} \qquad (1.43)$$

---

1. Blander: Molten Salt Chemistry, ed. Blander, Interscience (1964)

where $(p_1)_i$, is the partial pressure of the associated species $(M_1)_i$.

At equilibrium:

$$\mu_1(\text{liquid}) = \mu_1(\text{vapour}) \tag{1.44}$$

and the chemical potential of one mole of component 1 in the vapour is given by:

$$\mu_1(\text{vapour}) = \frac{(p_1)_1}{\sum i(p_1)_i}(\mu)_1 + \frac{(p_1)_2}{\sum i(p_1)_i}(\mu)_2 + \ldots$$

$$= \frac{\sum (p_1)_i (\mu)_i}{\sum i(p_1)_i} \tag{1.45}$$

where $(\mu)_i$ = chemical potential of the associated species (provided the non-ideality of the vapour is due to the association only)

$= RT \ln (p_1)_i$

and $\frac{(p_1)_i}{\sum i(p_1)_i}$ = the number of moles of species i per mole of $M_1$.

Since the system is in equilibrium:

$$(\mu)_1 = \tfrac{1}{2}(\mu)_2 = \tfrac{1}{3}(\mu)_3 = \ldots\ldots \text{ etc.} \tag{1.46}$$

From 1.45, 1.46:

$$\mu_1(\text{vapour}) - (\mu)_1 = \frac{1}{i}(\mu)_i \tag{1.47}$$

Hence:

$$\mu_1 - \mu_1^{\circ} = RT \ln \frac{(p_1)_1}{(p_1^{\circ})_1}$$

$$= \frac{RT}{i} \ln \frac{(p_1)_i}{(p_1^{\circ})_i} \tag{1.48}$$

$$= RT \ln a_1$$

Hence, provided the partial pressure of one species containing only component 1 is known, $a_1$ can be calculated. At low pressures, eqn. 1.48 is valid for component 1, independently of all other species in the vapour.

There are three main methods of determining the vapour pressure of fused salts:

1. Measurement of the boiling point of the pure molten single component or mixed salts[1,2]. This method is applicable for vapour pressures $> 10^{-3}$ atmos.

2. Transpiration method[3,4]. Here the vapour pressure of the salt is determined from the amount of salt vapour condensed from a known quantity of saturated carrier gas ($10^{-9}$ - $10^{-3}$ atmos).

3. Effusion method[5-8] ($< 10^{-9}$ atmos).

b) Cryoscopic measurements

Cryoscopic measurements have been used for determining the degree of dissociation in dilute mixtures where the activity

---

1. Bloom, Bockris, Richards and Taylor: J. Am. Chem. Soc., 80 2044 (1958)
2. Barton and Bloom: J. Phys. Chem., 60 1413 (1956)
3. Bloom and Welch: J. Phys. Chem., 62 1594 (1958)
4. Sense and Stone: J. Phys. Chem., 62 1411 (1958)
5. Langmuir: Phys. Rev., 2 329 (1913)
6. Knudsen: Ann. Physik., 28 75, 299; 29 179 (1909)
7. Berkowitz and Chupka: Ann. N.Y. Acad. Sci., 79 1073 (1960)
8. Porter and Schoonmaker: J. Chem. Phys., 29 1070 (1958)

coefficients are unity[1]. The Claussius-Clapeyron equation can be applied to the equilibrium between the solid phase of component 1 and a dilute solution of component 2, i.e.,

$$\frac{d \ln p_1/p_1^{\circ}}{dT} = \frac{L_f}{RT^2} \qquad (1.49)$$

where $p_1$ and $p_1^{\circ}$ are the vapour pressures of component 1 over the solution and the pure liquid respectively and $L_f$ is the molar heat of fusion at the melting point of component 1. If the molten system obeys Raoult's law, then $p_1/p_1^{\circ} = N_1$, so that eqn. 1.49 may be rewritten as:

$$\frac{d \ln N_1}{dT} = \frac{L_f}{RT^2} \qquad (1.50)$$

For most systems, Raoult's law is not applicable and therefore:

$$\frac{d \ln a_1}{dT} = \frac{L_f}{RT^2} \qquad (1.51)$$

If $a_1^{\circ}$, the activity of the pure liquid, is unity, then on integration one obtains:

$$\ln a_1 = -L_f \triangle T_f/RT_0T_1 \qquad (1.52)$$

where $T_1$ is the freezing point of the mixture, $T_0$ the freezing point of the pure solvent and $\triangle T_f = T_0 - T_1$.

In order that the integration is valid, $L_f$ is assumed to be independent of temperature and composition and hence eqn. 1.52 can only be applied to dilute solutions of mutually soluble salts.

---

1. See for example: Van Artsdalen: J. Phys. Chem., 60 172 (1956)

The activity of a component has also been determined from fusion diagrams[1,2], using the relationship:

$$\ln a_1 = \frac{\Delta H_\theta}{R}\left(\frac{1}{T} - \frac{1}{\theta}\right) + \frac{\Delta C_p}{R}\left[\ln\left(\frac{\theta}{T}\right) - \frac{\theta - T}{T}\right] \qquad (1.53)$$

where $a_1$ is the activity of the component in the mixture that separates on cooling, $\Delta H_\theta$ and $\theta$, represent the heat and temperature of fusion of this component in its pure state and $\Delta C_p$ the difference between the molar heat capacities of the component in its solid and liquid states. $\Delta C_p$ is assumed to be constant. Eqn. 1.53 holds only in the absence of mixed crystals and chemical compounds separating on cooling. A simplified formula can also be used when calorimetric data is unavailable[3].

$$\ln a_1 = \frac{\Delta H_\theta}{R}\left(\frac{1}{T} - \frac{1}{\theta}\right) \qquad (1.54)$$

Generally the calculation of the temperature correction for the activity requires knowledge of the partial molar heat of solution of component 1, a quantity seldom known. The recalculation at a given temperature can be made[3] by assuming the system to behave as a regular solution, i.e.,

$$RT \ln \frac{(a_1)}{(N_1)} = B\,(1-N_1)^2 \qquad (1.55)$$

where B is a constant. From this expression is obtained the equation[4]:

$$\log a'_{(T_2)} = \frac{T_1}{T_2} \log a_{(T_1)} + \frac{T_2 - T_1}{T_2} \log N_1 \qquad (1.56)$$

---


1. Murgulescu and Sternberg: Rev. Chem. l'Acad. R.P.R., 3 55 (1958)
2. Sternberg: ibid., 3 77 (1958)
3. Rey: Discuss. Faraday Soc., 4 257 (1948)
4. Murgulescu and Sternberg: Discuss. Faraday Soc., 32 107 (1961)

where $a'_{(T_2)}$ and $a_{(T_1)}$ are the activities at the absolute temperatures $T_2$ and $T_1$ respectively.

The main merit of this method of investigation, as opposed to e.m.f. determinations (see later), is that the activities in the systems, such as binary nitrates, and mixtures of alkali halides having a common cation (e.g. KBr and KCl), where formation cells are difficult to realise, are capable of estimation.

c) The equilibrium distribution of a solute between two immiscible solvents

This method has been used by Heymann et al.[1], but has limited applicability to molten salts because the phenomenon of immiscibility between molten salts is not common.

d) Electromotive force measurements

(i) Formation cells

Consider the cell:

$$\overset{1}{A(l)/AX_2(l)}\ (N_1) + \overset{2}{MX(l)/C,X_2(g)}\ (N_2)$$

where $AX_2$ is a divalent metal halide (mole fraction $N_1$) and MX an alkali metal halide (mole fraction $N_2$) and where the electrodes A(l) and $X_2(g)$ are reversible to $A^{2+}$ and $X^-$ ions respectively. The electrode reactions are:

---

1. Heymann, Martin and Mulcahy: J. Phys. Chem., 47 473 (1943)

$A \longrightarrow A^{2+} + 2e^-$ at the metal electrode

$X_2 + 2e^- \longrightarrow 2X^-$ at the halogen electrode

Thus the overall cell reaction is:

$$A(l) + X_2(g) \longrightarrow AX_2(l)$$

i.e. the formation of $AX_2$ from its elements.

Let $E^o$ be the e.m.f. of the cell when the mole fraction of $AX_2$ (component 1) is equal to unity (i.e. pure $AX_2$), the metal is in its standard state and the pressure of halogen (assumed to behave as a perfect gas) is one atmosphere. Let $E_1$ be the e.m.f. of the cell when the mole fraction of $AX_2$ is $N_1$ and the electrodes in their standard states as before. For pure $AX_2$ the free energy of formation $\triangle G^o$, is related to the e.m.f. $E^o$ by the equation:

$$\triangle G^o = -zFE^o \qquad (1.57)$$

where z is the number of electrons transferred in the formation of one mole of $AX_2$ and F is the Faraday.

In a mixture for which the mole fraction of component 1 is $N_1$, the free energy of formation $\triangle G_1$ is given by:

$$\triangle G_1 = -zFE_1 \qquad (1.58)$$

Hence from 1.57, 1.58:

$$-zF(E_1-E^o) = \triangle G_1 - \triangle G^o$$

$$= \triangle \bar{G}_1 \qquad (1.59)$$

where $\triangle \bar{G}_1$ is the partial molar free energy of $MX_2$. The relationship between $\triangle \bar{G}_1$ and the activity of $AX_2$ is given by the expression:

$$\triangle \bar{G}_1 = RT \ln a_1/a^o \qquad (1.60)$$

But since the activity in the standard state of component 1 is chosen as unity, eqn. 1.60 becomes:

$$\Delta\bar{G}_1 = RT \ln a_1 \qquad (1.61)$$

and from eqn. 1.59:

$$-zF(E_1-E^o) = RT \ln a_1$$
$$E_1 = E^o - \frac{RT}{zF} \ln a_1 \qquad (1.62)$$

Hence the activity of the component with respect to which the electrodes are reversible, can be determined by equation 1.62. The activity $a_2$, of the second component MX, can be determined by graphical integration of the Gibbs-Duhem equation in the form:

$$\log \gamma_2 = \int_0^{N_1} N_1/N_2 \; d \log \gamma_1 \qquad (1.63)$$

where $\gamma_1$ and $\gamma_2$ are the activity coefficients of $AX_2$ and MX respectively.

The use of this method for the determination of the activities of the components in molten salt solutions, is limited according to the availability of suitable reversible electrodes. Formation cells have been used in the present investigation.

(ii) Concentration cells

Consider the concentration cell with transference:

$$\begin{array}{c|c} \overset{1}{A(1)/AX_2(1)} & \overset{1}{AX_2(1)} + \overset{2}{MX(1)/A(1)} \\ N_1 = 1 & N_1 \qquad N_2 \end{array}$$

where A, $AX_2$ and MX have the same significance as before. The e.m.f. of this cell, where the mole fraction of component 1 in the right hand cell is $N_1$, is given by the expression:

$$E'' = -\frac{RT}{zF} \ln a_1 + \varepsilon \qquad (1.64)$$

where $a_1$ is the activity of $AX_2$ in the mixture and $\mathcal{E}$ is the diffusion potential between pure $AX_2$ and the mixture. (Here the activity of pure $AX_2$, $a^o$, is assumed to be unity as before.) By comparison of 1.64 with 1.62 it can be seen that:

$$\mathcal{E} = E'' - (E_1 - E^o) \qquad (1.65)$$

where E'' refers to the cell with transport and $(E_1-E^o)$ to the cell without transport.

Hence, provided the value of the diffusion potential is known, the activity of $AX_2$ can be evaluated. Murgulescu and Sternberg[1] have assumed $\mathcal{E}$ to be zero and have obtained reasonable agreement between the activities calculated from formation and concentration cells[2,3] for systems such as: AgCl-KCl, AgBr-KBr. Easteal[4] has found the diffusion potential to be very significant in studies on the binary lead/alkali halides. Therefore, unless $\mathcal{E}$ can be determined accurately, concentration cells do not provide a reliable method for the calculation of activities.

(iii) Oscillographic measurements

The thermodynamic activity of the components cannot be determined for mixtures of the alkali halides either by formation or concentration cells, owing to the difficulty in obtaining reversible alkali metal electrodes. This difficulty can be overcome[1] by

---

1. Murgulescu and Sternberg: Discuss. Faraday Soc., 32 107 (1961)
2. Murgulescu and Marchidan: Rev. Chem. l'Acad. R.P.R., 3 69 (1958)
3. Murgulescu and Marchidan: J. Phys. Chem. Russ., 34 2534 (1960)
4. Easteal: Ph.D. thesis, University of Tasmania (1964)

building up formation cells with preliminary electrolysis and measuring the back e.m.f. after the current is cut off. Such cells have been constructed[1,2] for the silver halides*, i.e.,

Ag/Ag hal (melt)/C, hal. (hal = Cl, Br, I.)

For temperatures between 450-600°C, the back e.m.f., measured by an oscillographic method[1] was found to be independent of the current density in the range 6.1-2.0 amps./cm.$^2$ and practically equal to the e.m.f. of the above reversible formation cell. Murgulescu and Sternberg[3] have suggested this method as a means of measurement of activity from normally impractical formation cells.

---

* For such a cell the e.m.f. can also be measured in the normal way without oscillographic techniques, e.g. Hildebrand, Salstrom, etc., (see Section 1.8).

1. Murgulescu, Sternberg, Medintev and Mustetea: Electrochim. Acta., 8 65 (1963)

2. Sternberg and Marchidan: Z. Physik. Chem., (Leipzig), 218 250 (1961)

3. Murgulescu and Sternberg: Discuss. Faraday Soc., 32 107 (1961)

## 1.7 CALCULATION OF THERMODYNAMIC QUANTITIES FROM THE E.M.F.'S OF FORMATION CELLS

Consider the cell:

$$\underset{N_1}{A(1)/AX_2(1)} + \underset{N_2}{MX(1)/C,\ X_2(g)}$$

a) For pure $AX_2$

The standard free energy of formation $\triangle G^o$ of pure $AX_2$ is given by equation 1.57, i.e.,

$$\triangle G^o = -zFE^o \quad \text{cal/mole} \tag{1.66}$$

where F is the Faraday (23,062 cal/volt equivalent), $E^o$ the e.m.f. of the cell containing pure $AX_2$ and z the number of electrons involved in the formation of one mole $AX_2$.

The standard entropy of formation $\triangle S^o$ is given by:

$$\triangle S^o = -zF dE^o/dt \quad \text{cal/deg/mole} \tag{1.67}$$

where $dE^o/dt$ is the rate of change of e.m.f. with temperature of the cell containing pure $AX_2$.

The heat, $\triangle H^o$, for the reaction, $A(1) + X_2(g) \longrightarrow AX_2(1)$, is given by:

$$\triangle H^o = \triangle G^o + T \triangle S^o$$

$$= zF\ (T\ dE^o/dt - E^o) \quad \text{cal/mole} \tag{1.68}$$

where T is the absolute temperature.

b) For $AX_2 + MX$

(Mole fraction of $AX_2$ is $N_1$ and the mole fraction of MX is $N_2$). We have:

$$\Delta G_1 = -zFE \quad \text{cal/mole} \tag{1.69}$$

$$\Delta S_1 = zF\, dE/dt \quad \text{cal/deg/mole} \tag{1.70}$$

$$\Delta H_1 = zF\,(T\, dE/dt - E) \quad \text{cal/mole} \tag{1.71}$$

where E, $\Delta G_1$, $\Delta S_1$ and $\Delta H_1$ have the same significance as before but are apprppriate to the mixture and not the pure salt. The difference between these thermodynamic quantities (i.e. $\Delta Z_1 - \Delta Z^o$) represent the change in the property resulting from the transfer of one mole of $AX_2$ from the standard state to a solution of concentration $N_1$. Thus the partial thermodynamic functions are given by:

$$\Delta \bar{G}_1 = \Delta G_1 - \Delta G^o = -zF\,(E - E^o)$$

(from 1.62)
$$= RT \ln a_1 \quad \text{cal/mole} \tag{1.72}$$

$$\Delta \bar{S}_1 = \Delta S_1 - \Delta S^o = zF(dE/dt - dE^o/dt) \quad \text{cal/deg/mole} \tag{1.73}$$

$$\Delta \bar{H}_1 = \Delta H_1 - \Delta H^o = \Delta \bar{G}_1 + T\, \Delta \bar{S}_1 \quad \text{cal/mole} \tag{1.74}$$

If the components form an ideal solution, then the value for $a_1$ will be the ideal activity, which, in the case of binary systems is represented by the mole fraction of component 1. Thus for binary systems, criteria of ideality are:

$$\Delta \bar{G}_1 \text{ (ideal)} = RT \ln N_1 \quad \text{cal/mole} \tag{1.75}$$

$$\Delta \bar{S}_1 \text{ (ideal)} = -R \ln N_1 \quad \text{cal/deg/mole} \tag{1.76}$$

$$\Delta \bar{H}_1 \text{ (ideal)} = 0 \tag{1.77}$$

The differences between these values and the calculated quantities (1.72-1.74) are called the excess partial thermodynamic quantities. The magnitudes of the excess thermodynamic quantities give a measure

of the deviations from ideal solution behaviour. Thus:

$$\Delta\bar{G}_1^{E} = \Delta\bar{G}_1 - \Delta\bar{G}_1 \text{ (ideal)}$$

$$= RT \ln \gamma_1 \qquad (1.78)$$

where $\gamma_1 = a_1/N_1$, is the activity coefficient of component 1.

$$\Delta\bar{S}_1^{E} = \Delta\bar{S}_1 - \Delta\bar{S}_1 \text{ (ideal)}$$

$$= zF\,(dE/dt - dE^{o}/dt) + R \ln N_1 \qquad (1.79)$$

$$\Delta\bar{H}_1^{E} = \Delta\bar{H}_1 \qquad (1.80)$$

The integral values of the thermodynamic quantities are estimated by graphical integration, by use of the equation[1]:

$$\Delta Z = (1-N_1) \int_0^{N_1} \frac{\Delta\bar{Z}_1}{(1-N_1)^2}\, dN_1 \qquad (1.81)$$

where $\Delta Z$ and $\Delta\bar{Z}_1$ are any integral and partial thermodynamic function of state.

The thermodynamic data for the other component MX, in the mixture of MX and $AX_2$ may be found from the expression:

$$\Delta Z = N_1 \Delta\bar{Z}_1 + N_2 \Delta\bar{Z}_2 \qquad (1.82)$$

---

1. Lantratov and Shevlyakova: Zh. Priklad. Khim., 34 1065 (1961)

## 1.8 REVIEW OF PREVIOUS WORK ON CHEMICAL CELLS

Most of the earlier work on formation cells was carried out by Hildebrand, Salstrom et al.[1-6], on cells of the type:

$$Ag/AgX,\ MX/X_2\ (p = 1\ atmos)\ graphite,$$

where M = Li, Na, K, Rb. Results were explained in terms of the melts acting as regular solutions, where:

a) The entropy increase is the same as for an ideal solution, i.e.,

$$\Delta\bar{S}_1 = -R \ln N_1, \quad \Delta\bar{S}_2 = -R \ln N_2;$$

b) The excess partial free energies of the components ( $\Delta\bar{G}_1^E$ and $\Delta\bar{G}_2^E$) change with composition in direct proportion to the square of the mole fraction of the other component, i.e.,

$$\Delta\bar{G}_1^E = b_1.N_2^2, \quad \Delta\bar{G}_2^E = b_2N_1^2 \qquad (1.83)$$

where $b_1$ and $b_2$ are constants.

It was assumed[7] that the ions of both the pure components and the salt mixtures, arrange themselves in a definite order, reminiscent of the crystal lattice. Hildebrand and Ruhle[1], in measuring the e.m.f. of the cell:

$$Pb/PbCl_2(N_1) + KCl(N_2)/C,\ Cl_2$$

---


1. Hildebrand and Ruhle: J. Am. Chem. Soc., 49 722 (1927)
2. Salstrom and Hildebrand: ibid., 52 4641 (1930)
3. Salstrom and Hildebrand: ibid., 52 4650 (1930)
4. Wachter and Hildebrand: ibid., 52 4655 (1930)
5. Salstrom: ibid.; 53 1794 (1931); 53 3385 (1931); 54 2653, 4252, 4257 (1932); 55 1029 (1933); 55 2426 (1933); 56 1272 (1934)
6. Salstrom, Kew and Powell: ibid., 58 1848 (1936)
7. Hildebrand and Salstrom: ibid., 54 4257 (1932)

with a chlorine electrode prepared by polarization, found that the activity of lead chloride exhibited negative deviations from ideal values and postulated the existence of complex ions, $Pb_2Cl_5^-$, $PbCl_4^{2-}$ and $PbCl_6^{4-}$. The e.m.f. of the cell:

$$Pb/PbCl_2 + PbBr_2/C, Br_2$$

was measured by Hildebrand and Salstrom, with a bromine electrode made by passing bromine over a graphite rod. A negative excess partial free energy for $PbBr_2$ was observed.

Voskresenskaia[2] has expressed the view that two salts forming a continuous series of solid solutions yield melts which are closest to ideal solutions. This is in contrast to the deductions of Salstrom[3], who found a positive partial excess free energy of AgBr in the system AgBr-NaBr, although the components formed a continuous series of solid solutions. This phenomenon has also been observed in the systems AgBr-LiBr[4], AgCl-LiCl[5], $MgCl_2$-LiCl[6] and $PbBr_2$-$ZnBr_2$[7]. The excess negative partial free energy of $PbBr_2$ in the system $PbBr_2$-$PbCl_2$, may be explained by postulating a reaction involving the exchange of anions between $PbCl_2$ and $PbBr_2$ and the subsequent formation of PbBrCl[8].

---


1. Salstrom and Hildebrand: J. Am. Chem. Soc., 52 4641 (1930)
2. Voskresenskaia: Izv. Sektora. Fiz-Khim. analiza, Akad.Nauk., S.S.S.R., 23 155 (1953)
3. Salstrom: J. Am. Chem. Soc., 53 1794 (1931)
4. Salstrom and Hildebrand: J. Am. Chem. Soc., 52 4650 (1930)
5. Salstrom, Kew and Powell: ibid., 58 1848 (1936)
6. Markov, Delimarskii and Panchenko: Zh. Fiz. Khim., 29 51 (1955)
7. Salstrom: J. Am. Chem. Soc., 55 1029 (1933)
8. Delimarskii and Markov: Electrochem. of Fused Salts, Sigma Press (1961)

Bloom and Richards[1] have investigated the activities of lead and cadmium chlorides in mixtures with sodium and potassium chlorides, using combinations of two types of cells:

a) concentration cells with liquid junctions of the type:

$$A(l)/ACl_2(l) + MCl(l) \;\vdots\; ACl_2(l)/A(l)$$

b) gas cells with liquid junctions of the type:

$$A(l)/ACl_2(l) \;\vdots\; ACl_2(l) + MCl(l)/C,\ Cl_2$$

where A refers to $Cd^{2+}$ or $Pb^{2+}$ and M to $Na^+$ or $K^+$. When connected back to back, these cells are together equivalent to the formation cell:

$$A(l)/ACl_2(l) + MCl(l)/C,\ Cl_2$$

Although information regarding the diffusion potential at the liquid junction can be obtained, this does not result in a satisfactory method for the measurement of activities compared to direct e.m.f. measurements on formation cells, as two sets of measurements must be carried out; this involves two sources of error.

Lantratov and Shevlyakova [2,3] have calculated thermodynamic quantities from the e.m.f's of formation cells, for molten salt system involving measurements of lead and cadmium halides with sodium and potassium halides, but the information derived regarding the nature of the melt is sparse. Other Russian workers[4] have calculated thermodynamic data for $PbCl_2$, $CdCl_2$ and $ZnCl_2$ in their solutions with the chlorides of K, Na, Li and Ba. Deviations from ideal solution

---

1. Bloom and Richards: To be published: Richards: Ph.D. thesis, University of New Zealand (1956).
2. Lantratov and Shevlyakova: Russ. J. Inorg. Chem., 4 523 (1959); 6 95 (1961)
3. Lantratov and Shevlyakova: Zh. Priklad. Khim., 34 1065, 2570 (1961)
4. Alabyshev and Lantratov: Trudy Leningrad Politekh. Inst. im M.I. Kalinina Elektromet. Tsvetnykh Metal, 93 (1957)

behaviour are found to increase with decreasing radius of the divalent metal ion. These workers state that this behaviour is related to the increase in the stability of the complex ions present in these melts.

Recently e.m.f. measurements have been conducted on three component systems. The association constants, $K_1$ and $K_2$, for the formation of $PbBr^+$ and $PbBr_2$, were evaluated from the data from molten mixtures of $NaNO_3$ and $KNO_3$[1]. For equimolar mixtures of $NaNO_3$ and $KNO_3$ at 240°C, the constants $K_1$ and $K_2$ were found to be 250 and 125 (in mole fraction units). Variation of the composition of the solvent changed the value of the association constants in such a way as to indicate an increasing strength of bonding as the proportion of $KNO_3$ increased - an effect similar to that in the system $AgNO_3$ - NaBr - $NaNO_3$[2].

Delimarskii and Roms[3], in investigating the ternary eutectic $PbCl_2$ - KCl - NaCl, found the e.m.f. of the cells:

Pb/48 : 36 : 16 mole % $PbCl_2$ - KCl - NaCl/C, $Cl_2$

to be not linearly dependent on the temperature - an effect in contrast to the behaviour of normal binary molten salt mixtures. Further e.m.f. measurements of three component systems have been completed[4,5], but to date, little structural information has been deduced from such investigations.

---


1. Manning, Blander and Braunstein: J. Inorg. Chem., 2 345 (1963)
2. Manning, Bansal, Braunstein and Blander: J. Am. Chem. Soc., 84 2028 (1962)
3. Delimarskii and Roms: Ukr. Khim. Zh., 29 781 (1963)
4. Storonkin, Shul'ts and Bushueva: Fiz. Khim. Rasplavlen. Solei i Shlakov. Acad. Nauk. S.S.S.R. Ural'sk. Filial. Inst. Elektrokhim Tr. Vses Soveshch Sverdlovsk 177 (1960)
5. Bushueva and Shul'ts: Vestn. Leningr. Univ. 18 Ser. Fiz. i Khim. 160 (1963)

The only application of formation cells to reciprocal salt systems has been carried out by Bloom and Welch[1], in order to calculate the activity of $PbBr_2$ in the systems $PbBr_2$-NaCl and $PbCl_2$-NaBr. The cells used were:

$$\underset{N_1}{Pb/PbBr_2} - \underset{(1-N_1)}{NaCl/C, Br_2}$$

$$\underset{N_1}{Pb/PbCl_2} - \underset{(1-N_1)}{NaBr/C, Br_2}$$

Concentration cells of the type:

$$Ag \left| \begin{matrix} KNO_3 \\ AgNO_3 \end{matrix} \right| \begin{matrix} KNO_3 \\ AgNO_3 \\ KCl \end{matrix} \left| Ag \right.$$

have been used by Blander et al.[2-4] for calculation of the activity of $AgNO_3$ and comparison of the values obtained thereby with those predicted on the basis of the quasi-lattice model for reciprocal molten salt systems[4].

Although this is by no means a complete summary of work done using fused salt formation cells, it is indicative of the use to which these cells have been put. Apart from the initial work done by Hildebrand and Salstrom it is not until recently that this method has been more extensively used in calculating thermodynamic properties of molten salt systems.

---

1. Bloom and Welch: Trans. Faraday Soc., 59 410 (1963)
2. Braunstein and Blander: J. Phys. Chem., 64 10 (1960)
3. Hill and Blander: J. Phys. Chem., 65 1866 (1961)
4. Blander: J. Phys. Chem., 63 1262 (1959)

## 1.9 OBJECTS OF THE PRESENT INVESTIGATION

Measurements of the electromotive force of formation cells have lead to conflicting results for not only the absolute values of the e.m.f. and thermodynamic quantities but also in the interpretation of these results in terms of interactions within the melt. In this investigation it was hoped to clarify and at the same time provide information regarding the nature of the species in various molten salt systems. This work has been divided into three parts - the formation cells employed contained three different classes of molten salt electrolytes:

a) binary ($AX_2$ + MX)

b) three component ($AX_2$ + MX + M'X)

c) reciprocal ($AX_2$ + MY)

For the binary systems it was intended to show the influence of alkali metal ions $M^+$, on the stability of complex ions in the molten mixtures $AX_2$ +MX and also to derive the activity of $AX_2$ theoretically.

In the three component systems it was hoped to find a relationship between the ratio of two different alkali metal ions $M^+/M'^+$ and the departures from ideal solution behaviour of the activity of $AX_2$ within these molten systems.

The reciprocal molten salt systems were investigated with the idea of comparing existing activity models with the experimental

activities of the components. It was intended to either substantiate or modify at least one of these models to explain the experimental results, or, in the event of no existing model being applicable to the systems investigated, to propose a new theory.

The following systems were investigated:

a) (i) $PbBr_2$ - KBr

(ii) $PbBr_2$ - RbBr

(iii) $PbBr_2$ - CsBr

using the cell:

$$Pb(l)/PbBr_2(l) + MBr(l)/C, Br_2(g)$$

b) (i) $PbCl_2$ - CsCl

(ii) $(x\ PbCl_2 + x\ CsCl)$ — $(1-2x)$ LiCl

(iii) $(x\ PbCl_2 + x\ CsCl)$ — $(1-2x)$ NaCl

(iv) $(x\ PbCl_2 + x\ CsCl)$ — $(1-2x)$ KCl

(v) $(x\ PbCl_2 + x\ CsCl)$ — $(1-2x)$ RbCl

(vi) $(2x\ PbCl_2 + x\ CsCl)$ — $(1-3x)$ LiCl

(vii) $(2x\ PbCl_2 + x\ CsCl)$ — $(1-3x)$ NaCl

(viii) $(2x\ PbCl_2 + x\ CsCl)$ — $(1-3x)$ KCl

(ix) $(2x\ PbCl_2 + x\ CsCl)$ — $(1-3x)$ RbCl

using the cell:

$$Pb(l)/PbCl_2(l) + CsCl(l) + MCl(l)/C, Cl_2(g)$$

c) (i) $CdBr_2$ + NaCl

(ii) $CdCl_2$ + NaBr

using the cells:

$$Cd\ .\ Sn(l)/CdBr_2(l) + NaCl(l)/C, Br_2(g)$$

and $$Cd\ .\ Sn(l)/CdCl_2\ (l) + NaBr(l)/C, Br_2(g)$$

# CHAPTER 2

# EXPERIMENTAL

## 2.1 APPARATUS

a) Furnace

The block of the electric resistance furnace consisted of a stainless steel tube 2" in external diameter, 1/16" in thickness and 17½" in length. It was wound with a coil of 19 B and S gauge Kanthal A.B. wire, of total resistance 39.0 ohms. The windings were insulated from the metal tube by 1/32" thick mica sheeting and were held in place by a ¼" coating of high alumina content ceramic cement. The furnace frame was constructed from 1" x 1" x 1/8" angle iron with overall dimensions 13" x 13" x 17". Around this was a case made from 3/8" "Sindanyo" asbestos sheeting. The case was packed with asbestos wool lagging. Four angle iron supports held the furance in a vertical position 3½" above bench level. The stainless steel tube was supported within the furnace by the "Sindanyo" ends. A 3/8" thick "Sindanyo" plate, 1 13/16" in diameter and 8½" from the bottom of the furnace, served to support the cell and to hold the indicator thermocouple (see Section 2.1b) in position. The plate was attached to the end of a 3/16" diameter stainless steel rod which passed through a 3/16" hole in the "Sindanyo" base of the furnace. It is evident that convection currents did not exist and hence a steady temperature was able to be maintained.

b) Temperature control and measurement

Power to the furnace was supplied from the 240 volt mains via an Ether Ltd. "Transitrol" (type 990) indicating temperature-controller and a "Variac" variable transformer. In practice the "Transitrol" served only as a temperature indicator because the best control offered by this was only about $\pm$ 2°C. The temperature sensing element was a chromel-alumel thermocouple, sited beside the base of the cell. For the precise temperature control required in the experimental measurements, the "Variac" was adjusted so that the rate of heating of the furnace at the required temperature, was balanced by the rate of loss of heat by radiation. The temperature could be controlled in this manner to within $\pm$ 0.2°C over a period of about one hour.

The furnace temperature was measured by means of a chromel-alumel thermocouple sheathed by a silica tube, the hot junction being immersed in the melt. The thermo electric force was measured with a "Tinsley" (type 3184 D) portable potentiometer. The thermocouple was calibrated at the following thermometric fixed points:

| | |
|---|---|
| M.Pt. KCl (A.R.) | 770.4°C |
| F.Pt. Zn (As Free) | 419.5°C |
| F.Pt. Pb (A.R.) | 327.5°C |
| F.Pt. Ag (electrolytically pure) | 960.5°C |
| F.Pt. Cd (99.995% pure) | 320.9°C |

c) Formation (or chemical) cells

The cell is a slightly modified version of that used by Richards[1]. All components were made from transparent silica supplied by Thermal Syndicate Ltd. Unless otherwise stated all silica tubing had wall thickness between 1/32" and 1/16".

The outer portion of the cell (see fig. 2.1) consisted of a 1 3/8" external diameter silica tube, sealed at one end and 12" long. 1½" from the top was a side arm, 1½" long and 15/32" external diameter. Since the upper end of this tube was above the furnace, the temperature was low enough to allow a rubber bung to be used to position the other components within this casing. The bung had to be replaced from time to time owing to halegen attack.

The 15" long reference half-cell was constructed from silica tubing, ½" in external diameter. A sintered silica disc, produced by Thermal Syndicate Ltd., of 3/8"-7/16" diameter and of known porosity (see Section 2.4c), was sealed into the tube ½" from the base, care being taken in the sealing to ensure that the central portions of the disc were not fused. Electrical contact with the pool of molten metal in the base of this half-cell was effected by a sheathed tungsten wire. Silica capillary tubing, approximately 18" long and ¼" in external diameter, was collapsed (by heating under vacuum) onto the wire, leaving about 3½" of unsheathed tungsten wire at the top end. Within the sealed portion, the tube was cut at right angles to a length of 16" and ground as illustrated in fig. 2.2, to

---

1. Richards: Ph.D. thesis, University of New Zealand (1956)

## Legend

Fig. 2.1

| | | |
|---|---|---|
| A | = | Side arm adapter for halogen electrode |
| $X_2$ | = | Halogen gas |
| P | = | Platinum wire to potentiometer |
| P' | = | Platinum screw |
| R | = | Rubber tubing |
| B | = | Rubber bung |
| C | = | Carbon rod |
| $S_1$ | = | Silica pot, housing electrodes |
| $S_2$ | = | Silica sheath around carbon rod |
| $S_3$ | = | Reference half-cell |
| D | = | Sintered disc |
| W | = | Tungsten wire to potentiometer |
| M | = | Molten metal |
| M' | = | Molten salt mixture |
| T | = | Thermocouple and sheath |
| T' | = | Thermocouple leads to potentiometer |

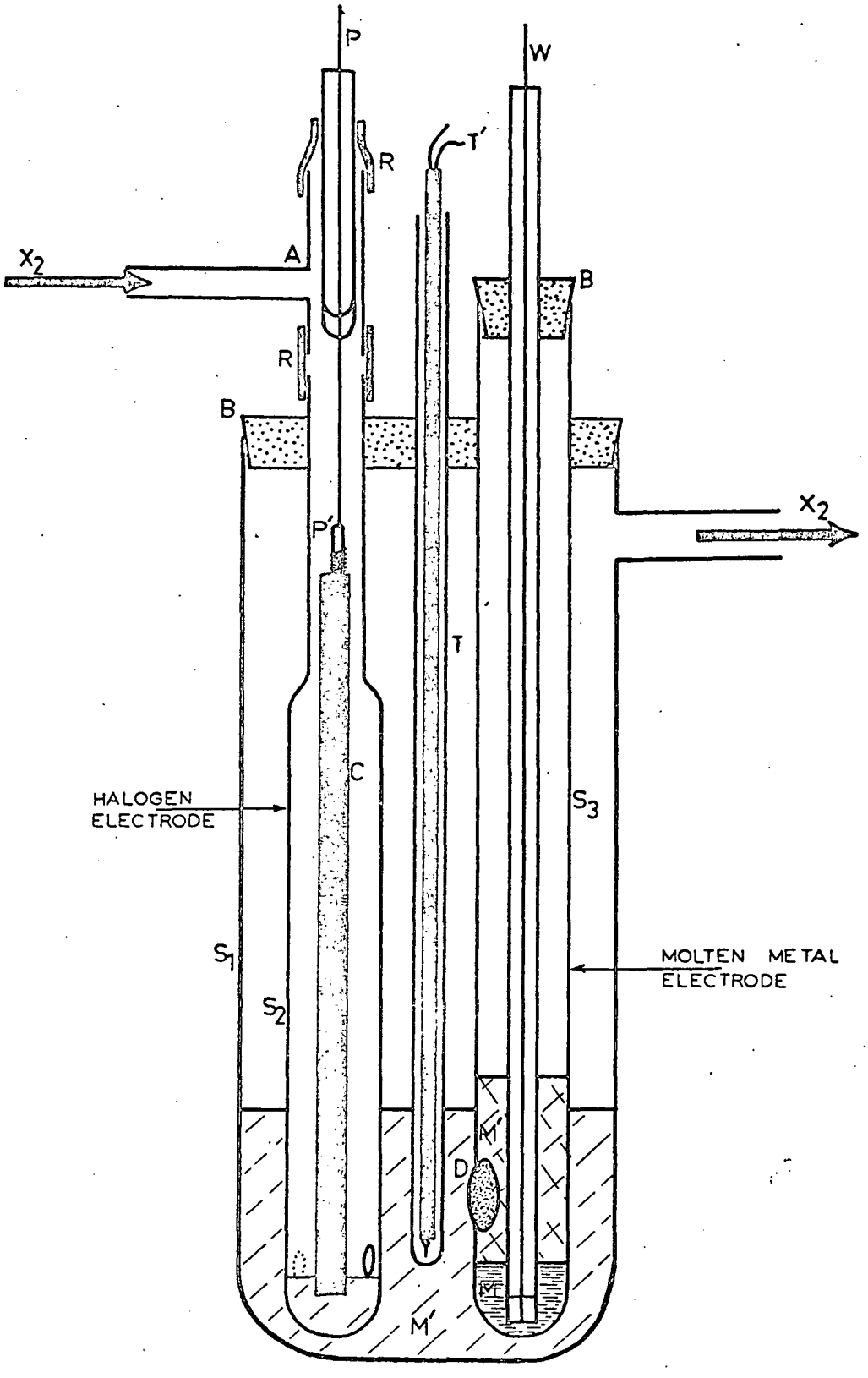



FIG. 2·1 DIAGRAMMATIC REPRESENTATION OF FORMATION CELL

expose approximately $^{3}/_{16}$" of tungsten wire. This was found to give the most satisfactory electrode, for other methods failed to produce effective seals and offered little structural protection to the tungsten wire. A copper wire clamped to the upper end of the tungsten wire made contact with the potentiometer.

The sheath for the carbon rod (see fig. 2.1) was made by joining a silica tube of $^{7}/_{16}$" external diameter and 8" in length, to another piece of silica of $^{11}/_{32}$" external diameter and 5½" in length. The free end of the larger tube was sealed and two holes, approximately $^{1}/_{8}$" in diameter, were blown in either side, ½" from the base of the tube, to allow escape of bromine and chlorine. The larger diameter portion of the sheath accommodated the slight swelling of the carbon rods in experiments with the cadmium systems. An adaptor, $^{11}/_{32}$" in external diameter and 2½" in length, for the admission of halogen, was attached to the top of the sheath by a short length of rubber tubing. Halogen gas was admitted half-way down this via a side arm, ¼" external diameter and 2" long.

Electrical contact between the carbon rod and the potentiometer was provided by the following arrangement: A threaded platinum rod ($^{1}/_{8}$" Whitworth) ½" long, welded onto the end of a length of platinum wire was screwed into a pretapped hole in one end of a carbon rod. This wire was sealed into a piece of pyrex tubing, ¼" in external diameter and $3^{3}/_{4}$" in length and the latter was positioned vertically in the side arm adaptor as shown in fig. 2.1. A short piece of rubber tubing at the top of the adaptor provided a seal to prevent the escape of halogen gas. A copper wire made contact

## Legend

Fig. 2.2

| | | |
|---|---|---|
| W | = | Tungsten wire |
| S | = | Silica capillary tubing |
| B | = | Region where silica is collapsed on tungsten wire |
| A | = | Ground portion |
| F | = | Flat surface exposing length of tungsten wire |

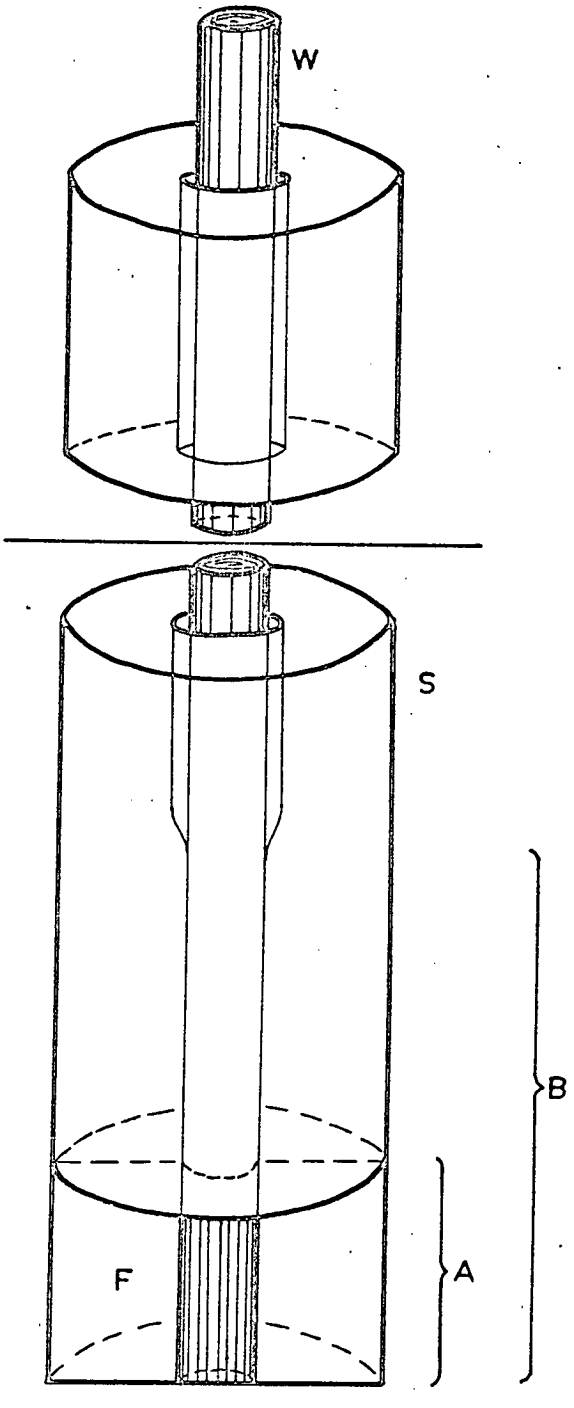



FIG. 2·2 ENLARGED VIEW OF SHEATHED TUNGSTEN WIRE

between the platinum wire and the potentiometer as before*.

Contained in the cell, in addition to the reference half-cell and the halogen electrode, were a thermocouple sheath of ½" external diameter and 13" long and an inlet tube, which allowed dry hydrogen halide to be passed in order to remove "oxy" compounds from the melt; the inlet tube had an external diameter of $^{3}/_{16}$" and a length of 14".

The silica used in construction of the cell was found to be resistant to attack by most salts. Only in the systems involving LiCl and NaCl was there any appreciable corrosion. In measurements involving lithium chloride, certain components of the cell (especially the reference half-cell) had to be replaced after each run. As a result of salt attack, the silica walls became considerably corroded and often resistant surface coatings were formed. Replacement was necessary for structural reasons and also to prevent contamination of successive mixtures.

d) Gas flow apparatus

The function of the gas flow apparatus (see fig. 2.3) was to ensure a constant flow of dry halogen gas at a known pressure.

Chlorine or bromine was admitted to the cell via a concentrated sulphuric acid gas washing bottle (to indicate flow rate) and a U-tube, $A_1$, packed with "anhydrone" drying agent and glass wool. "Suck-back" of the sulphuric acid to the halogen supply was prevented by the trap, $T_1$, and splashing of acid into the "anhydrone" tube was

---

* As both the W - Cu and Pt - Cu junctions were at room temperature, no thermo-e.m.f. due to these was introduced

## Legend

**Fig. 2.3**

| | | |
|---|---|---|
| $W_1$, $W_2$, $W_3$ | = | Two-way taps |
| $W_4$ | = | Three-way tap for admitting either argon or halogen gas to system |
| $W_5$ | = | Two-way bleeder tap to reduce pressure in system to atmospheric |
| $T_1$, $T_4$ | = | Traps to prevent suck-back |
| $T_2$ | = | Splash trap |
| $T_3$ | = | Glass wool trap to collect condensed salt vapour |
| S | = | Conc. $H_2SO_4$ flow rate indicator |
| $C_1$, $C_2$ | = | Halogen gas absorption traps |
| $A_1$, $A_2$ | = | "Anlydrone" drying tubes |
| M | = | Conc. $H_2SO_4$ manometer |

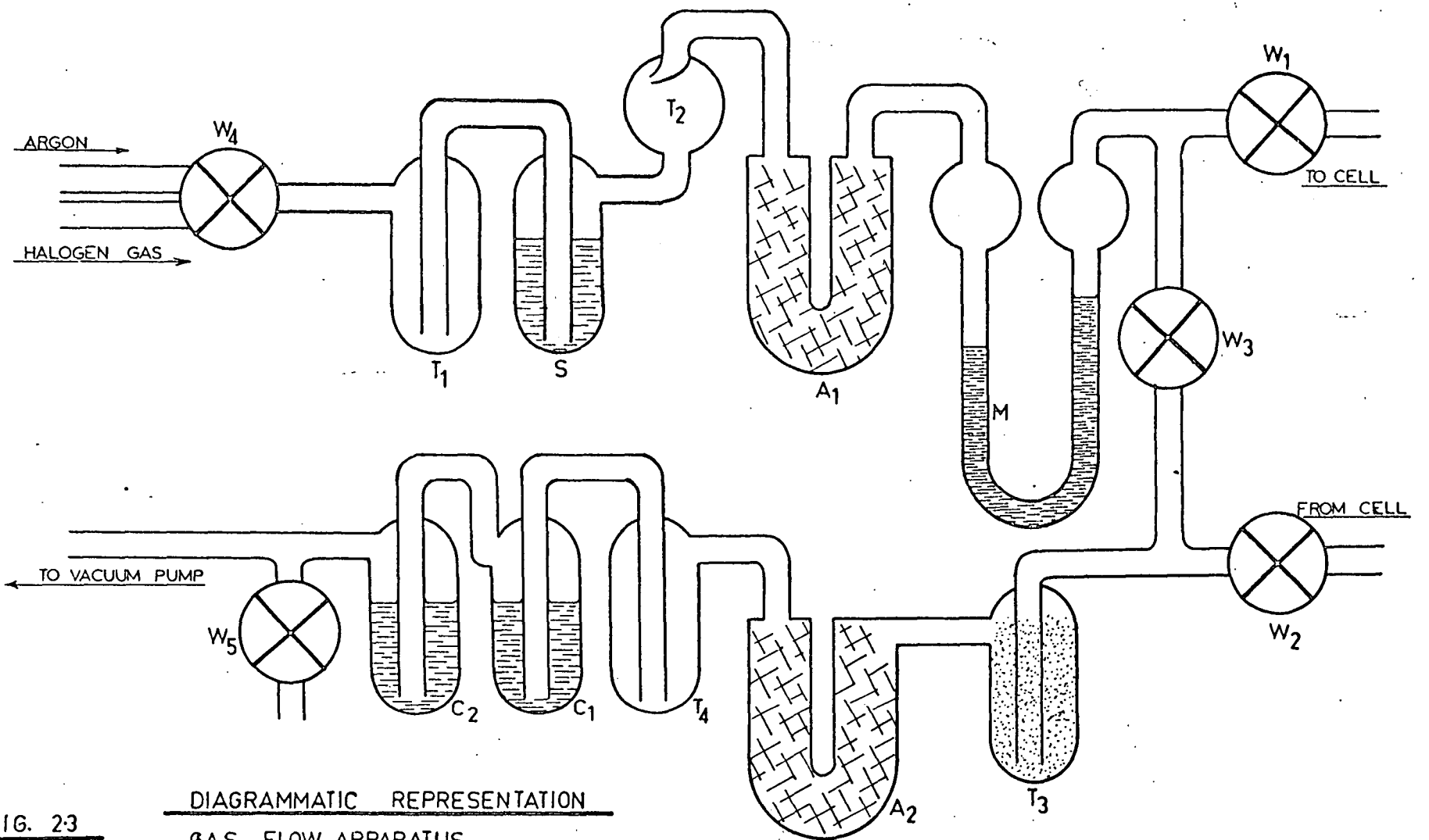



FIG. 2·3

DIAGRAMMATIC REPRESENTATION

GAS FLOW APPARATUS

eliminated by the splash bulb, $T_2$. The gas pressure was measured by a sulphuric acid manometer. As the levels in the two arms were equalised during measurements, knowledge of the acid density was unnecessary. Halogen from the cell first entered a glass wool trap, $T_3$, to collect the small amounts of salts volatilised from the melt and was finally absorbed in caustic soda solution. Halogen in excess of that absorbed was washed away via a water vacuum pump. A second "anhydrone" trap, $A_2$, prevented back diffusion of water vapour into the cell. Pyrex tubes fitted with "Ball and Socket" ground glass joints and connected to the gas flow system, conveyed halogen gas to and from the cell. Coupling to the cell was made with short lengths (approximately 1") of Teflon tubing. The joints and Teflon couplers allowed a certain degree of flexibility in the apparatus.

When the cell was not in operation taps $W_1$ and $W_2$ were closed, tap $W_3$ opened and dry, deoxygenated argon continually circulated through the gas flow apparatus. Although the argon used was specified as oxygen free, traces of oxygen were removed by passing the gas over a tightly wound roll of copper gauze, heated to 600°C by a small furnace. The oxide produced was reduced from time to time by the passage of hydrogen over the heated gauze.

All joints and taps were lubricated with silicone grease. Although attack by chlorine and bromine took place, this was relatively slow and surfaces required cleaning and regreasing after four or five experimental runs.

## 2.2 SOURCE OF CHLORINE AND BROMINE

Chlorine was supplied to the gas flow apparatus directly from a cylinder (see Section 1.5g).

Bromine was obtained in the same manner as by Welch[1]. The apparatus (see fig. 2.4) consisted of a sealed pyrex tube 1/32" thick, 1½" external diameter and 12" long. fitted with a ground glass cone at its extremity. On this cone was seated a ground glass socket, supporting a 7/8" external diameter pyrex tube, at the end of which a coarse sintered pyrex disc was fused. The two three-way taps allowed deoxygenated argon, either to be passed into the bromine, or to by-pass the transpirer for flushing purposes. The depth of bromine was usually about 8" to enable the carrier gas to become saturated with the halogen. Joints and taps were lubricated with silicone grease. The transpirer was connected to the gas flow system by means of pyrex tubing and ball and socket ground glass joints. It was kept at a constant temperature (about 15°C) by immersion in a water bath.

The lower the partial pressure of bromine, the smaller will be the measured e.m.f. and hence the larger the percentage error in the measured value. For greatest accuracy it was therefore desirable to have as great a partial pressure of bromine as possible.

---

1. Welch: Ph.D. thesis, University of New Zealand (1960)

## Legend

Fig. 2.4

B = Pyrex tube containing bromine - situated in constant temperature bath

C = Ground glass joint

S = Sintered glass disc

W = Three-way taps

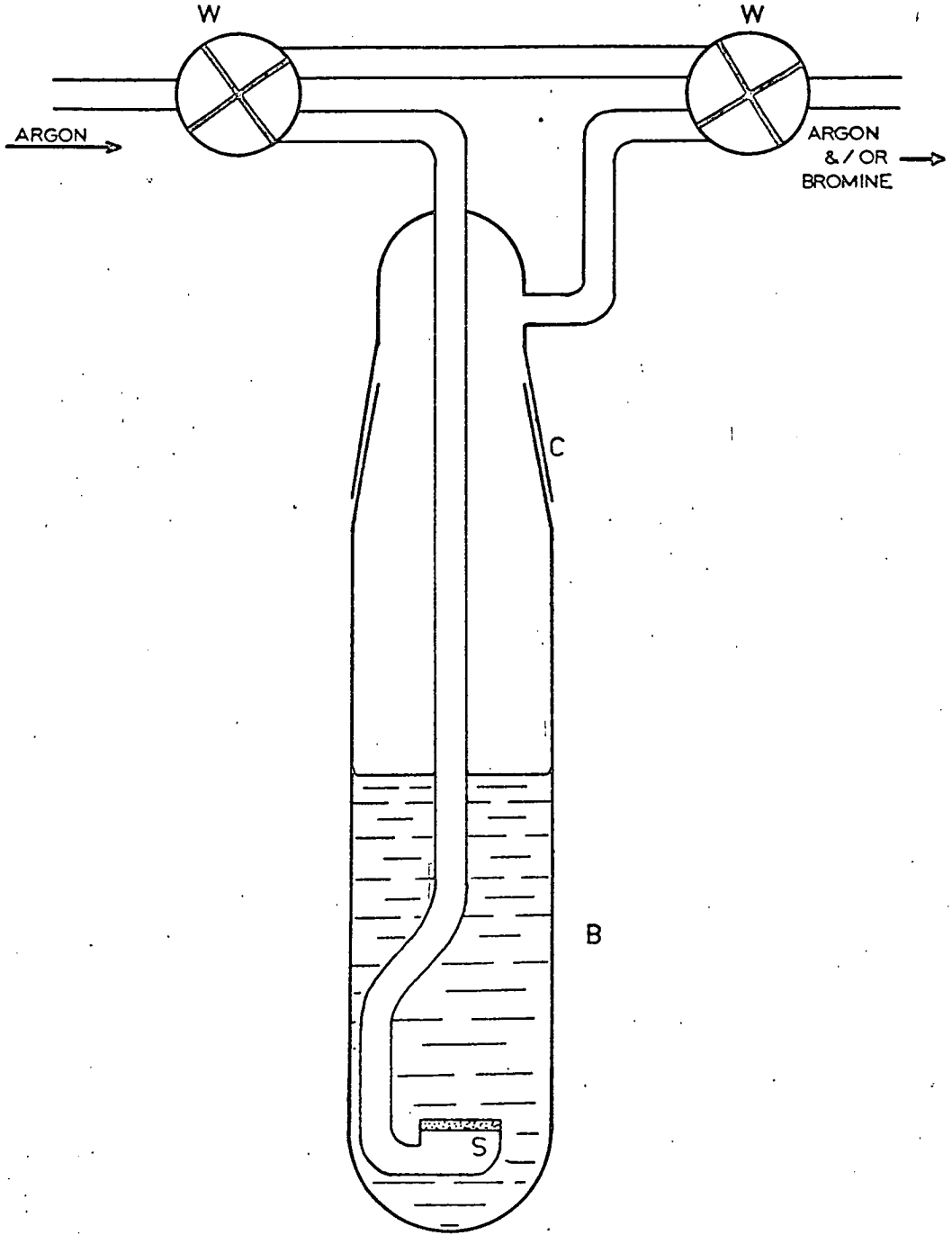



FIG. 2·4 THE BROMINE TRANSPIRER

## 2.3 EXPERIMENTAL PROCEDURE

Salt mixture which would melt to about 40 mls., was placed in the outer container of the cell, care being taken to expose the salt to the atmosphere for the minimum possible time. The various cell components were positioned within the rubber bung, the carbon rod adjusted within the silica sheath and the assembly lowered into the outer cell casing. When the salt had melted, the correct weight of metal (to give a volume of 0.5 mls.) was added to the reference half-cell, followed by sufficient salt mixture to give a head no greater than 0.5-0.7 cms. above the surrounding melt level, after all the cell components, including the sheathed tungsten wire, had been firmly fixed. Thus, any diffusion was mostly in the direction of the bulk electrolyte. During this assembly process, cell components were heated to 130-150°C before coming in contact with any of the mixtures in order to ensure the absence of water.

If the melted salt had solid oxy-halide in suspension, dry hydrogen chloride or hydrogen bromide as appropriate, was bubbled through the melt until the melt had cleared.

The hydrogen chloride or bromide tube was then closed to the atmosphere and the cell connected to the gas flow equipment. With a relatively fast initial halide flow rate (approximately 250 bubbles per minute), the furnace was allowed to reach the lowest temperature for the run. When the cell had attained thermal equilibrium, the gas flow rate was decreased to 60-70 bubbles per minute and the gas

pressure within the cell reduced to atmospheric by the bleeder tap ($W_5$ in fig. 2.3). The e.m.f. was recorded when constant to within $\pm$ 0.1 millivolts for approximately 4 minutes. Initially a period of about 1 hour (greater for the bromide electrode) elapsed between attainment of thermal equilibrium and stability of the e.m.f. For subsequent readings, the delay was usually of the order of 5 minutes. This delay was probably due to the period required for the melt to become saturated with halogen gas.

The furnace temperature was raised in a series of steps (approximately 20°C increments) and when the cell had reached equilibrium at each temperature the e.m.f. was noted. The prevailing atmospheric pressure was recorded from a Fortin barometer at each equilibrium position for the chloride systems. For the bromide systems, the temperature of the water bath was recorded, or, on a few occasions, the room temperature, when this was lower than the temperature of the water bath.

In this manner the cell e.m.f's were determined from 30-50°C above the melting points of the mixtures, over a temperature range of 150-200°C. For each reading taken, the internal resistance of the cell was also measured. If the resistance of the cell showed unexpected changes during any series of measurements, the run was repeated. Electromotive force readings were also recorded at decreasing temperatures. Such measurements showed a slight divergence (about 3 milivolts) from the measurements recorded at increasing temperature and these were attributed to slight composition

changes with time (e.g. volatilization of the more volatile component). Consequently e.m.f. measurements at increasing temperatures only, were recorded.

After the completion of measurements, the halogen gas was flushed from the cell by the passage of argon and the salt poured out. Samples from the bulk electrolyte and reference half-cell were kept for analysis. Between runs, the carbon rods were heated to a bright orange in an oxy-coal gas flame to volatilise all absorbed salt and then subjected to the treatment outlined in Section 1.4b. The carbon rods for a particular system were used in successive runs, until thinned by oxidation accompanying the heat treatment.

## 2.4 STANDARDIZATION OF APPARATUS

### a) Determination of the carbon-tungsten thermo e.m.f.

The thermo e.m.f. of the carbon-tungsten couple contributes to the total e.m.f. of the formation cell and must, therefore, be evaluated in order that the electromotive force, due to the cell reaction alone, can be determined.

A carbon rod and sheathed tungsten wire were positioned in the outer tube of the cell, in the same relative positions as in an experimental run. Contact between the two was made by a platinum wire, welded to the end of the tungsten wire and attached to the base of the carbon rod. This eliminated the electrode potentials encountered experimentally, in the systems studied. It was assumed that if the hot junction was at a certain temperature, the temperature gradients in the tungsten and the carbon would be the same in every cell.

The thermo e.m.f. was measured over a temperature range of 450-800°C. Results are tabulated in table 2.1 and a plot of the e.m.f. of the carbon tungsten couple vs. temperature is shown in fig. 2.5. The carbon lead of the couple is negative whereas in the formation cell the carbon electrode is the anode. Since the thermo e.m.f. operates in the opposite direction to the cell e.m.f., the correction must be added to the measured cell e.m.f.

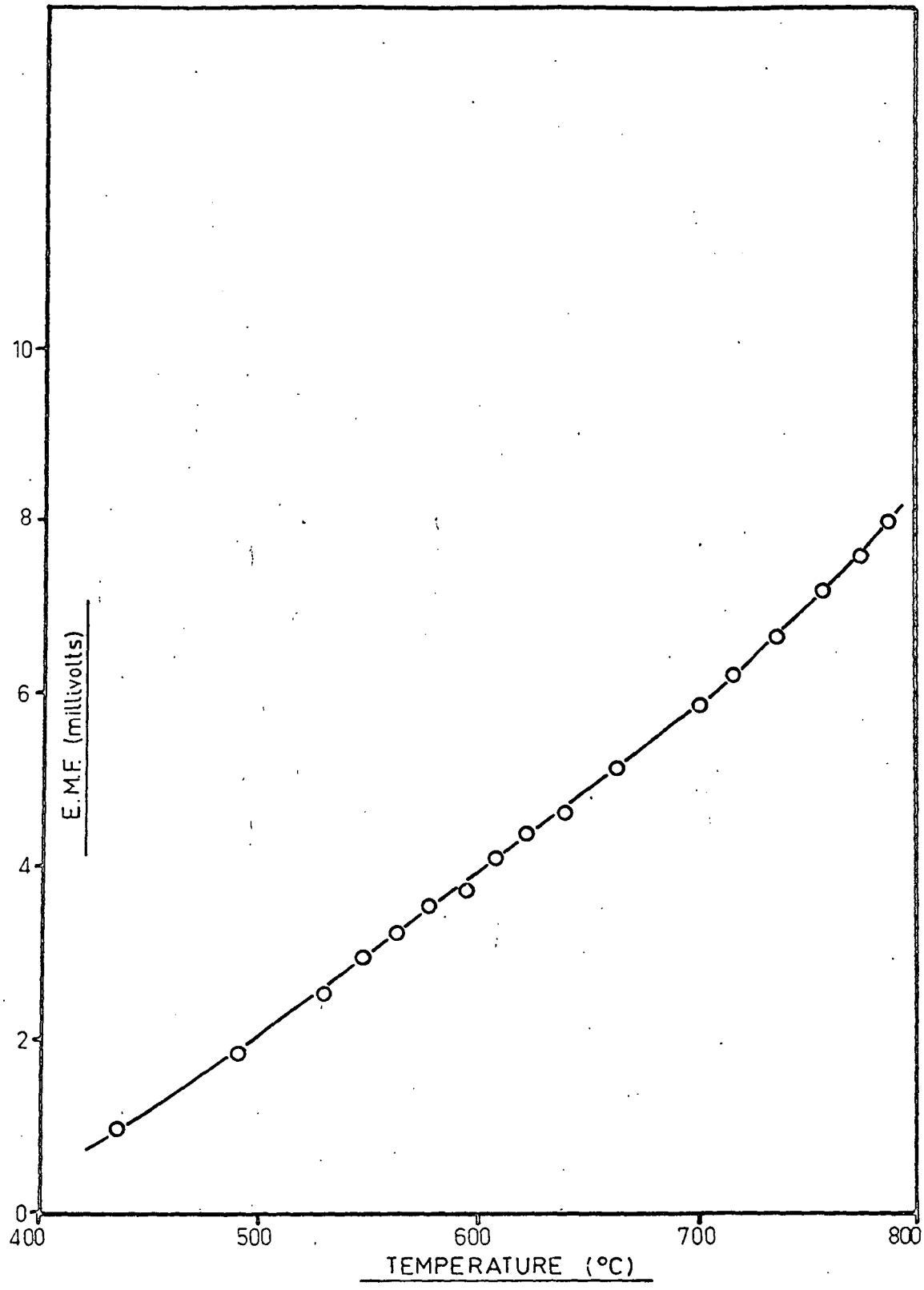



FIG. 2·5 E.M.F. vs TEMPERATURE PLOT FOR THE TUNGSTEN-CARBON COUPLE

TABLE 2.1

Thermo e.m.f. of the carbon-tungsten couple as a function of temperature

| temperature (°C) | C-W e.m.f. (m.v.) | temperature (°C) | C-W e.m.f. (m.v.) |
|---|---|---|---|
| 436.2 | 0.967 | 638.5 | 4.607 |
| 489.9 | 1.843 | 662.2 | 5.123 |
| 511.0 | 2.188 | 699.9 | 5.853 |
| 529.0 | 2.514 | 714.8 | 6.201 |
| 547.0 | 2.940 | 737.0 | 6.653 |
| 562.4 | 3.220 | 757.8 | 7.192 |
| 576.6 | 3.521 | 774.5 | 7.580 |
| 594.2 | 3.706 | 787.6 | 8.010 |
| 607.4 | 4.078 | 802.6 | 8.347 |
| 621.4 | 4.358 | | |

b) Choice and treatment of carbon rods

For all the lead systems, spectrographically pure soft graphite rods, 30 cms. long and 6.5 mms. in diameter were used. These were supplied by Johnson, Matthey Co. Ltd. For the cadmium reciprocal systems, this form of carbon was found to be less successful because of the tendency of the rods to swell. Harder rods from the same source were substituted as these were much more resistant to swelling. The disadvantage with these rods, compared to the rods used in the lead systems, was a slight increase in the time required for the halogen electrode to attain equilibrium.

## Legend

Fig. 2.6A

I = Halogen inlet

O = Halogen exit

C = Carbon rod

F = Furnace

Fig. 2.6B

W = Two-way tap

J = Ground glass joint

C = Carbon rod

D = Desiccant

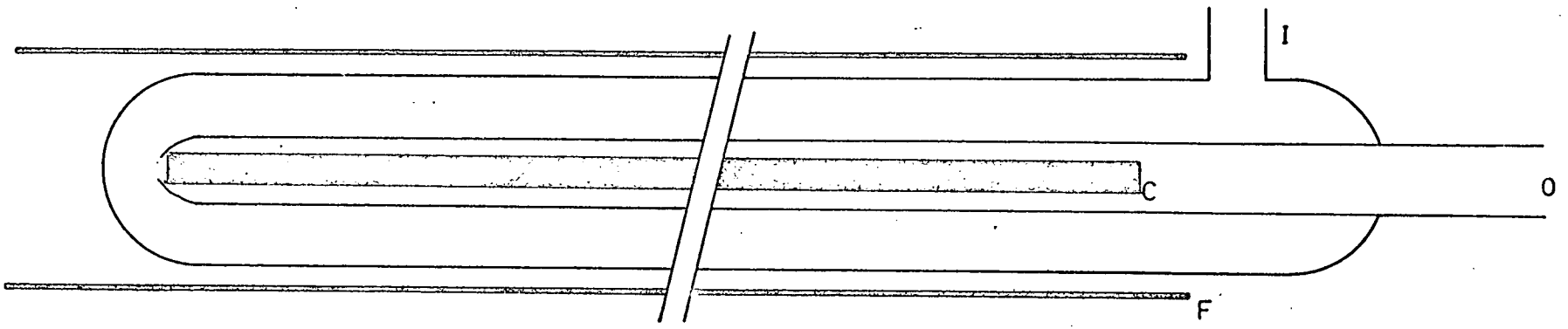



FIG. 2·6A CARBON ROD HALOGENATOR

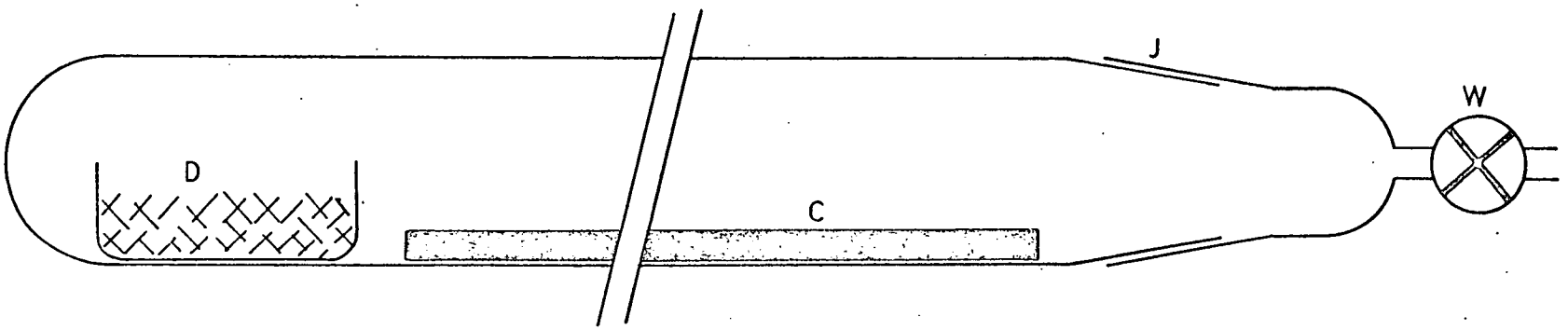



FIG. 2·6B DESICCATOR FOR CARBON ROD

To decrease the time required for the halogen electrode to reach equilibrium, the carbon rods for all the cells were presaturated with halogen gas. After salt had been volatilized from the carbon (see Section 1.3) they were placed in the tube shown in fig. 2.6a and connected to the gas flow apparatus. Chlorine or bromine gas, depending on the system, was passed through the tube for 1½ hours at about 600°C and then the tube was cooled to room temperature while continuing the passage of gas. The rods were then stored in a desiccator (see fig. 2.6b).

c) The internal resistance of the cell and the choice of silica discs

The function of the disc in the formation cell was merely to provide a means of separating the halogen gas from the metal electrode, but in so doing it was necessary that it did not influence the e.m.f. of the cell.

In order to keep atmospheric oxygen and moisture from the reference half-cell, the upper portion was sealed with a small rubber bung (see fig. 2.1). With increasing temperature however, the pressure of the enclosed gas above the melt in this half-cell, was sufficient to force salt into the bulk electrolyte via the disc. This was the case with coarse (porosity 1) discs. On such occasions, the volume of melt in the reference half-cell was reduced to approximately 1 ml. and was thereby subjected to relatively large composition changes. This condition was remedied by the use of very fine (porosity 4) discs, but

these produced a relatively high internal cell resistance (approximately 10,000 ohms), which lowered the sensitivity of the galvanometer and led to errors in the measured e.m.f. A further disadvantage of the porosity 4 disc was an increase in the cell resistance with time, possibly due to trapped air within the pores of the disc reacting with the electrolyte to form insoluble oxy-halide compounds which blocked the disc. It was found, however, that silica discs of porosity 2 or 3 were the best to overcome both high cell resistance and loss of electrolyte. These discs gave a cell resistance of approximately 30-50 ohms.

d) Reversibility of the chlorine and bromine electrodes

Earlier investigators, (see for example Salstrom and Hildebrand[1], and Welch[2]) using a cell similar to that employed in this work, have shown that a pure graphite electrode allows the following thermodynamic reaction to take place reversibly:

$$\tfrac{1}{2}X_2 + e^- \rightleftharpoons X^- \quad \text{(where X = Cl or Br)}$$

This was established by plotting log. $P_{Br_2}$ against the observed e.m.f. According to the Nernst equation which may be written as:

$$E_{obs.} = E^{o}_{PbBr_2} + RT/ZF \ln P_{Br_2} \qquad (2.1)$$

such a plot should produce a straight line. For this work the e.m.f. of the cell:

$$Pb(l)/PbBr_2(l)/C, Br_2(g)$$

---

1. Salstrom and Hildebrand: J. Am. Chem. Soc., 52 4641 (1930)
2. Welch: Ph.D. thesis, University of New Zealand (1960)

was measured at constant temperature (503°C) as the partial pressure of bromine was varied between 40 and 120 mms. Hg. The plot of log. $P_{Br_2}$ vs. e.m.f. yielded a straight line, which verified the reversibility of the bromine electrode. Experimental points showed a deviation from the straight line of no greater than ± 0.03%.

## 2.5 MATERIALS USED IN THE EXPERIMENTS

Throughout the text, the names of the various chemical manufacturers will be abbreviated as follows:

| | |
|---|---|
| Hopkin and Williams Ltd. | H. & W. |
| British Drug Houses Ltd. | B.D.H. |
| May and Baker Ltd. | M. & B. |
| L. Light and Co. Ltd. | LIGHT |
| New Metals and Chemicals Ltd. | N.M. & C. |
| By-products and Chemicals Pty. Ltd. | B.P. & C. |
| Ajax Chemical Pty. Ltd. | AJAX |
| Imperial Chemical Industries of Australia and New Zealand Ltd. | I.C.I. |

### a) Alkali halides

The alkali halides were of the highest quality available and were used without further purification. Following is a list of the alkali halides used, together with the manufacturer and the purity of the chemical:

RbCl : N.M. & C., greater than 99.7% pure
" : LIGHT, not less than 99.9% pure
CsCl : N.M. & C., greater than 99.5% pure
" : LIGHT, not less than 99.9% pure
KCl : B.P. & C., "Univar" grade, not less than 99.8% pure
NaCl : B.P. & C., "Univar" grade, not less than 99.9% pure
LiCl : B.D.H., "Laboratory reagent" grade, not less than 98.5% pure
CsBr : N.M. & C., "pure"
RbCl : N.M. & C., 99.7% pure
KBr : M. & B., "analar" grade

b) Lead chloride

(i) The method of Bloom and Heymann[1]:

Lead chloride was precipitated from an aqueous solution of M. & B., "analar" grade lead nitrate, with a slight excess of AJAX "analar" grade hydrochloric acid. The precipitate was washed with distilled water and evaporated to dryness in the presence of conc. HCl. The solid was then rewashed thoroughly with cold water, recrystalised from hot water and dried at 120°C.

(ii) B.D.H. "Laboratory reagent" grade lead chloride, of not less than 99% purity, was recrystalised from boiling water.

Analysis of the lead chloride prepared by both methods gave an assay of 99.9%.

c) Lead bromide

An analagous procedure to 1.5(b)(i) for lead chloride, was used with M. & B. "analar" grade hydrobromic acid. Here the precipitated bromide was not evaporated with excess HBr as this process tended to decompose the salt. The analysis of $PbBr_2$ corresponded to a purity of 99.8%.

d) Cadmium chloride

Cadmium chloride was prepared by direct combination of molten cadmium and chlorine gas, using the method described by Barton et al.[2]

---

1. Bloom and Heymann: Proc. Roy. Soc., A188 392 (1947)
2. Barton, Bloom and Richards: Chemistry and Industry 439 (1956)

Cadmium metal was supplied by the Electrolytic Zinc Company, Tasmania, and was specified as 99.995% pure.

It was imperative that air was excluded at all times in the procedure, to prevent the formation of oxy-chlorides. This was ensured by a constant flow of oxygen/gas free through the apparatus. When all the cadmium metal and cadmium sub-chloride had been converted to $CdCl_2$, the melt was poured out into preheated silica basins and immediately stored in an evacuated desiccator to lessen the time of exposure to the atmosphere. It was found that a better quality cadmium chloride was produced, if, after the cadmium had melted and the exothermic reaction between metal and chlorine started, only slight external heat was applied. Continued vigorous heating, apart from decreasing the rate of reaction, tended to produce relatively large quantities of oxy-chlorides. Analysis of samples of $CdCl_2$ taken from each batch, gave a range in purity of not less than 99.3-99.8% $CdCl_2$.

e) Cadmium bromide

Cadmium bromide was prepared by direct combination of molten cadmium metal and bromine as above. Here however, the halogen gas was transferred to the reaction flask by transpiring heated liquid bromine with deoxygenated argon. Analysis of samples of cadmium bromide taken from each batch, gave a range in purity of not less than 99.4-99.7% $CdBr_2$.

f) Bromine

Distillation of the "analar" grade bromine supplied by M. & B. was the only purification carried out. The specified purity was not less than 99.5% w/w and the maximum impurity (chlorine) was present to the extent of not more than 0.05% w/w.

g) Chlorine

This was supplied by I.C.I. and was not further purified before use.

h) Lead metal

Both H. & W. and B.D.H. "analar" foil were used without further purification.

i) Tin and cadmium alloy

B.D.H. "analar" grade granulated tin and cadmium supplied by the Electrolytic Zinc Co., Tasmania, were alloyed in equimolar ratio, poured into small pyrex fusion tubes and allowed to solidify. Any oxide formed in the melting process was left in the alloying vessel Subsequent oxidation was prevented by sealing the upper end of the tube until the alloy was required for use.

## 2.6 PREPARATION OF MIXTURES

In all cases, salts were weighed as the calculated amounts of the anhydrous components, according to the relationship:

$$N_1 = \frac{W_1/M_1}{W_1/M_1 + W_2/M_2 + \ldots W_n/M_n} \qquad (2.2)$$

where $N_1$, $W_1$, $M_1$ are the mole fraction, weight and molecular weight of component 1 etc. The salts were mixed by melting and poured into preheated silica basins. The solidified melts were ground finely while hot to ensure complete homogenuity, since one component often separated first, in the cooler regions of the container on cooling. Binary and three component lead mixtures were stored in an oven at 120°C, while mixtures of the reciprocal cadmium systems were kept in vacuum desiccators until required.

## 2.7 ANALYSIS OF MIXTURES

In the binary lead bromide-alkali metal bromide systems, it was found sufficient to analyse for lead alone. In the three component lead chloride-alkali metal chloride systems, it was necessary to analyse for both chlorine and lead in order to obtain the composition of the mixtures. For the reciprocal cadmium halide-alkali metal halide systems it was necessary to analyse for cadmium and either the total halogen or else both chlorine and bromine, depending on the procedure chosen. Volumetric techniques were used in all cases. It must be pointed out that in the following analyses for lead and cadmium, although accurate and reliable estimations were obtained, a great deal of experience was required for the estimation of the end points.

### a) Analysis for lead as $Pb(NO_3)_2$ using Solochrome Red B indicator

This method is similar to that mentioned by Price[1]. A sample of the lead halide mixture containing approximately 1 gm. $PbBr_2$ or $PbCl_2$ was weighed out accurately. This was dissolved in 50 : 50 concentrated nitric acid/water and evaporated to dryness beneath a drying lamp. This evaporation procedure was slow, but prevented loss of solution by bumping. When the evolution of hydrogen halide had ceased, the resulting lead nitrate was acidified with two drops of dilute nitric acid and made up to 250 mls. with distilled water. 25 ml. aliquots of this solution were then titrated

1. Price: Comprehensive analytical chemistry, ed. Wilson & Wilson, Elsevier Pub. Co., (1962)

with standardised sodium molybdate (approx. 6.0 gms. per litre) using solochrome red B 125 as indicator. Titrations were repeated until three consecutive titres agreed to within 0.02 mls. From the titre of sodium molybdate, the mole fraction of lead halide in the mixture could be evaluated. The $Na_2MoO_4 . 2H_2O$ used was B.D.H. "analar" grade material.

Both in this and in succeeding standardisations of the titrating solution, the standard solution employed consisted of a solution of the salt being analysed (e.g. a standard solution of $CdBr_2$ for analysis of the system $CdBr_2$ - NaCl). In this way corresponding end points for unknown and standard solutions could be obtained.

b) Analysis for lead as lead chloride using diphenyl carbazone as indicator(1)

The above procedure (1.7a) was lengthy because of the evaporation step and so the following method was preferred. The end points in this and the proceeding method were equally reproducible. The binary bromide mixtures could not be analysed by this method, as bromide ions interfered with the absorption indicator and no definite end point could be obtained.

A salt sample containing approximately 1 gm. $PbCl_2$ was dissolved in hot concentrated ammonium acetate solution and made up to 250 mls. with distilled water when cool. A 25 ml. aliquot of this

---

1. Method suggested by - Duhrosvkaya and Filippova: Zavod. Lab., 21 523 (1955)

solution was acidified with glacial acetic acid and titrated with standardised $Na_2MoO_4 . 2H_2O$ (approximately 6.0 gms. per litre), using diphenyl carbazone as indicator. Titrations were repeated until agreement to within 0.02 mls. was obtained. From the titre of sodium molybdate, the weight of lead chloride in the mixture could be calculated.

c) Analysis for chloride using dichlorofluorescein indicator

A sample containing about 0.4 gms. chloride was dissolved in boiling concentrated ammonium acetate as before (boiling water in the case of cadmium chloride) and made up to 250 mls. An aliquot, of volume governed by the total chloride present, was acidified with two drops of glacial acetic acid and titrated with standardised silver nitrate solution (approximately 15 gms. per litre), using dichlorofluorescein as indicator. Titrations were carried out under artificial lights to prevent decomposition of the resulting AgCl precipitate due to sunlight; such decomposition obscured the end point.

d) Analysis of the three component mixtures: $PbCl_2$ - CsCl - MCl

The composition of a binary mixture containing a common anion, may be determined by volumetric estimation of the anion. Consider the system AB + CB:

Let W = total weight of B from analysis

" $M_1$ = molecular weight of AB

" $M_2$ = molecular weight of CB

Let $W_1$ = weight of AB present in sample

" $W_2$ = weight of CB present in sample

" $W_3$ = total weight of sample for analysis

= $W_1 + W_2$

" A = atomic weight of B

Then total weight of B (= W) is given by:

$$W = \frac{W_1 A}{M_1} + \frac{W_2 A}{M_2}$$

$$= \frac{(W_3 - W_2)A\,M_2 - W_2 A M_1}{M_1 M_2}$$

On rearrangement:

$$W_2 = \frac{M_2(W_3 A - W M_1)}{A(M_2 - M_1)} \qquad (2.3)$$

Consider the system $PbCl_2$ - CsCl - MCl (M = Li, Na, K, Rb):

(i) Weight of $PbCl_2$ in sample

The weight of lead chloride ($W_3$) was obtained by volumetric estimation of lead with standardised sodium molybdate and diphenyl carbazone as indicator.

(ii) Weight of MCl in sample

Let W = total weight of chloride in sample - obtained by titration with standardised $AgNO_3$ solution

" $M_1$ = molecular weight CsCl

" $M_2$ = molecular weight MCl

" $M_3$ = molecular weight $PbCl_2$

" $W_1$ = weight of CsCl in sample

" $W_2$ = weight of MCl in sample

Let $W_3$ = weight of $PbCl_2$ in sample

" $W_4$ = total weight of sample for analysis

= $W_1 + W_2 + W_3$

" $W_5$ = total chloride present in $PbCl_2$ from lead analysis

" A = atomic weight chlorine

Then from eqn. 2.3:

$$W_2 = \frac{M_2\left[(W_4 - W_3)A - (W - W_5)M_1\right]}{A(M_2 - M_1)} \qquad (2.4)$$

and $W_1 = W_4 - (W_2 + W_3)$ (2.5)

Hence the mole fractions of each component can be calculated.

e) Analysis of reciprocal cadmium halide systems

(i) The method of Barton, Bloom and Richards[1] for the analysis of binary cadmium mixtures, was found to be equally applicable to reciprocal cadmium mixtures. The experimental technique was altered however, to give improved end point determinations.

Consider a standard solution of $CdCl_2$ containing a gms. $CdCl_2$ per b mls. of solution.

Let C = aliquot taken for analysis

" M = molecular weight of $CdCl_2$

" $S_1$ = titre of NaOH for standard $CdCl_2$

" $S_2$ = titre of $AgNO_3$ for standard $CdCl_2$

" x = titre NaOH for unknown sample

" y = titre $AgNO_3$ for unknown sample

" z = weight of sample

1. Barton, Bloom and Richards: Analyst, 81 245 (1956)

Then from the NaOH titration:

$$\text{Number of moles } CdCl_2 \text{ present} = \frac{ab}{CM} \cdot \frac{x}{S_1} \qquad (2.6)$$

$$= \text{number of gm. atoms cadmium}$$

$$\text{and number gm. atoms chlorine} = \frac{2ab}{CM} \cdot \frac{x}{S_1} \qquad (2.7)$$

$$= \text{number of gm. atoms bromine}$$

From the $AgNO_3$ titration:

$$\text{Total number of gm. atoms chlorine} = \frac{2ab}{CM} \cdot \frac{y}{S_2} \qquad (2.8)$$

$$= \text{total number gm. atoms bromine}$$

The NaOH titration gives the total amount of halogen associated with cadmium. The excess halogen, i.e., 2.8-2.7 must be that associated with the alkali halide.

$$\therefore \text{ Excess halogen} = \frac{2ab}{CM}\left[\frac{y}{S_2} - \frac{x}{S_1}\right] \qquad (2.9)$$

$$= \text{number of moles NaX}$$

$$\text{mole fraction } CdY_2 = \frac{\text{No. moles } CdY_2}{\text{No. moles } CdY_2 + \text{No. moles NaX}}$$

$$= \frac{\frac{ab}{CM} \cdot \frac{x}{S_1}}{\frac{ab}{CM} \cdot \frac{x}{S_1} + \frac{2ab}{CM}\left[\frac{y}{S_2} - \frac{x}{S_1}\right]}$$

which on simplification yields:

$$\text{mole fraction } CdY_2 = \frac{x}{2\left[\frac{S_1}{S_2}\right]y - x} \qquad (2.10)$$

This is equivalent to the Barton et al. equation.

A salt sample of 0.1 to 0.2 gms. was dissolved in about 25 mls. of distilled water. The total halide (Br + Cl), was estimated by method 1.7c. Dichlorofluorescein gave the end point when all the chloride had been precipitated; the bromide having the lower solubility

product was precipitated first. At the completion of the titration, the solution, together with the precipitated silver halide, was transferred to a Buchner funnel and filtered under vacuum. The precipitate was washed well with distilled water and the filtrate transferred to a 250 ml. beaker where it was tested for neutrality with methyl red indicator. After the solution had been made up to 125-150 mls., it was heated to 85-90°C to prevent the formation of basic cadmium compounds and then titrated with standardised NaOH solution containing approximately 4 gms. NaOH per litre. It has been found[1] that under these conditions $Cd(OH)_2$ precipitates quantitatively. The pH. theshold for precipitation of cadmium as cadmium hydroxide is 7.6[2] and precipitation may be considered to be complete at pH. 10. Thymol blue, with a pH. range 8.0-9.6, was used as indicator and found to give a much more satisfactory end point than the thymol phthalein used by Barton et al.[3] About 15 drops of thymol blue (0.2 gms. per 250 mls. of 80% ethyl alcohol/water) was used, the colour change being from yellow to blue. The sodium hydroxide titre was corrected for the blank end point correction by repeating the titration with hot distilled water.

Removal of the precipitated silver halide was necessary for the production of a clearly visible end point. By test analyses on known samples, no less of accuracy occured due to the possible retention of $Cd^{2+}$ ions by this precipitate.

---

1. Coetzee: J. Chem. Soc., 997 (1951)
2. Britton: Ann. Rep. Chem. Soc., 40 43 (1943)
3. Barton, Bloom and Richards: Analyst, 81 245 (1956)

(ii) Separate estimation of chlorine and bromine was also achieved quantitatively. In this method, about 3.5-4.0 gms. of salt were weighed out accurately, dissolved in warm water and made up to 250 mls. Chloride and bromide were estimated potentiometrically using a differential method of analysis. Two coiled silver wires were employed as electrodes. One electrode was enclosed in a separate compartment to which was attached a rubber bulb; connection between this compartment and the bulk solution was via a capillary tube. A 10 ml. aliquot of the solution containing the ions $Cd^{2+}$, $Na^{+}$, $Cl^{-}$ and $Br^{-}$, was transferred to a 250 ml. beaker and diluted to about 150 mls. Standardised silver nitrate was added 1 ml. at a time, the e.m.f. recorded and the composition of the electrolytes in the two compartments equalised using the bulb. As the end point of the titration for either bromide or chloride ions was approached, each aliquot of $AgNO_3$ was progressively decreased to about 0.03 ml.

The condition of the electrodes was important in regard to the rate at which equilibrium electrode potentials were attained. The most satisfactory treatment was found to be as follows:
Electrodes were cleaned in hot concentrated nitric acid. Silver was then electrodeposited on these as cathodes, from a solution of 1% $AgNO_3$ in 90% methanol/water, for 1 hour, with a current of 3 milliamps. A platinum wire sealed in glass functioned as the anode. Electrodes were then washed in distilled water and assembled in the titration vessel.

At the completion of each potentiometric titration, the silver chloride/bromide precipitate was filtered off and cadmium estimated as in 1.7e(i).

Although the second method for mixed halide estimation was very precise, it was also time consuming and the no less accurate first method was preferred. Inaccuracies introduced in weighing out salt samples, due to contamination by air and water vapour, were absent in the first method.

Salt samples taken before and at the completion of runs were all stored in small wax-sealed containers until required for analysis. (Lead salt samples were stored in an oven at 120°C until required.)

## 2.8 COMPOSITION CHANGES

### a) Sublimation effects

In all the lead halide systems studied, with the exception of the system $PbBr_2$-KBr, composition changes during experimental runs were no greater than $\pm$ 0.1 mole % $PbX_2$. For the system $PbBr_2$-KBr, the greater range (300°C) over which the e.m.f. was measured, contributed to greater composition changes; these changes were no greater than $\pm$ 0.5 mole % $PbBr_2$. Variations in the mole % of $CdBr_2$ and $CdCl_2$ in the reciprocal systems were no greater than $\pm$ 0.3 mole %.

### b) Solubility of metal in salt

The solubility of metallic lead in all lead systems, combined with sublimation effects in the reference half cell, contributed to an error of no greater than $\pm$ 0.3 mole % $PbX_2$. The greater solubility of liquid cadmium in the reciprocal systems gave a composition error of no greater than $\pm$ 0.7 mole % $CdX_2$.

# CHAPTER 3

# PRESENTATION OF RESULTS

## 3.1 THE BINARY SYSTEMS $PbBr_2$-MBr (M = K,Rb,Cs)

### a) Pure $PbBr_2$

The e.m.f. $E^o$, of the formation cell containing pure lead bromide, was measured over the temperature range 460°-730°C; the cell may be represented by:

$$Pb(l)/\text{pure } PbBr_2(l)/C,\ Br_2(g)$$

The e.m.f. measurements are recorded in Table 3.1 and are plotted in fig. 3.1. Values obtained by previous workers are also indicated in the same figure. Values of e.m.f. for this and all the following systems, have been corrected for both the carbon-tungsten thermo e.m.f. and for the partial pressure of bromine.

The values obtained by Lantratov and Shevlyakova[1] show considerable scatter about the calculated "line of best fit"; deviations range from 25 millivolts at 320°C, to 70 millivolts at 560°C. The curved nature of the line, especially at temperatures above 500°C, indicates that the e.m.f. of the cell is made up of at least two temperature dependent contributions - that due to the cell reaction and possibly that due to variations in the nature of the cell components, e.g., electrolyte, electrodes, etc.

The form of the halogen electrode used by Lantratov and Shevlyakova, relies on the evaporation of bromine from a reservoir of liquid bromine above the graphite rod. Because the temperature of this

---

1. Lantratov and Shevlyakova: Russ. J. Inorg. Chem., 4 523 (1959)

reservoir will, to some extent, be affected by the temperature of the cell, it is likely that the partial pressure of $Br_2$ at the electrode will change as the cell temperature is varied. This will result in a non-linear dependence of the cell e.m.f. on temperature.

By analogy with the case of pure lead chloride (see Section 3.2a) it may be argued that the curved plot of e.m.f. vs. temperature could be due to depression of the partial pressure of bromine by the salt vapour. From the vapour pressure data of Bloom et al.[1], however, the pressure of $PbBr_2$ above the pure salt at 550°C is only about 2.5 mms. and this would have negligible effect on the partial pressure of halogen, unless the latter partial pressure was very small.

The solubility of lead metal in molten lead chloride has been estimated at about 0.05%[2]. It is possible, therefore, that the method of Lantratov and Shevlyakova[3] of using a capillary to separate $Pb/PbBr_2$ and $PbBr_2/C, Br_2$ half cells could allow chemical interaction between the dissolved bromine and dissolved lead by mixing in this capillary tube. This could affect the reversibility of the $Pb/Pb^{2+}$ and $Br_2/Br^-$ electrodes.

The results of Welch[4], uncorrected for the partial pressure of the bromine electrode, show far less scatter than those of Lantratov and Shevlyakova[3]. The former have been recalculated by the

---

1. Bloom, Bockris, Richards and Taylor: J. Am. Chem. Soc., 80 2044 (1958)
2. Corbett: Fused Salts, ed. Sundheim, McGraw Hill Book Co., (1964)
3. Lantratov and Shevlyakova: Russ. J. Inorg. Chem., 4 523 (1959)
4. Welch: Ph.D. thesis, University of New Zealand (1960)

present author for $P_{Br_2}$ = 760 mm. (see fig. 3.1) and they show reasonable agreement with this work. The slope of the line, however, is more consistent with the work of Salstrom[1], where the absolute values at corresponding temperatures are approximately 0.01 volts higher.

The present values of $E^o$ for the cell with pure lead bromide are reproducible with both increasing and decreasing temperatures and the points show a mean deviation of not more than 0.2 mv. from the line of best fit. The line is represented by the equation:

$$E^o = 1.2813 - (5.275 \times 10^{-4})t$$

where t is the temperature in °C. Thermodynamic properties of pure lead bromide are listed in Table 3.2.

b) The system $PbBr_2$-KBr

Variations of the e.m.f. of the formation cells with temperature for each of five mixtures, are presented in Table 3.3. The equations to the lines of best fit, calculated by the method of least squares, are listed in Table 3.4 and plotted in fig. 3.2. Isotherms of e.m.f. vs. composition are shown in fig. 3.3. For some reason the results for the cell containing 19.7 mole % $PbBr_2$ seem to be rather anomalous, for not only is the gradient of the line inconsistent with the mixtures richer in lead bromide, but also thermodynamic data etc. for the system $PbBr_2$-KBr, in this region, shows a difference in trend from the other binary $PbBr_2$ mixtures. This does not necessarily mean that the e.m.f./temperature relationship for this composition is in error but this possibility must be considered in the

---

1. Salstrom: J. Am. Chem. Soc., 54 2653 (1932); 55 1029 (1933)

discussion of the system.

Values for the activity and activity coefficient of $PbBr_2$ at different compositions, are listed in Table 3.5 for three temperatures. The values for KBr, calculated from the graphical integration of the Gibbs-Duhem equation at 600°C, are shown in Table 3.6. Corresponding quantities are plotted in fig. 3.4. The error in $a_{PbBr_2}$ is estimated as ranging from $\pm$ 0.0015 units at 0.2 mole fraction $PbBr_2$ to $\pm$ 0.007 units at 0.8 mole fraction $PbBr_2$, whereas that for $a_{KBr}$, because of the uncertainty in extrapolating to infinity in the graphical estimation, is approximately $\pm$ 0.03 units for compositions in excess of 0.60 mole fraction $PbBr_2$ and as high as $\pm$ 0.08 units for 0.20 mole fraction $PbBr_2$.

Partial molar thermodynamic quantities for $PbBr_2$ are tabulated in Table 3.7 and are plotted in figs. 3.5-3.7. Integral thermodynamic functions, obtained by graphical integration of equation 1.81 and partial thermodynamic functions for KBr derived using equation 1.82, are listed in Table 3.8 and represented graphically in figs. 3.5 and 3.6. Assuming the uncertainty in the e.m.f. of the formation cells to be within $\pm$ 0.3 mv., then the uncertainty in the thermodynamic functions can be estimated as follows:

| | |
|---|---|
| $\Delta G_1$ $\pm$ 15 cals/mole, | $\Delta \bar{G}_1, \Delta \bar{G}_1^E$ $\pm$ 20 cals/mole, |
| $\Delta S_1$ $\pm$ 0.2 cals/deg/mole, | $\Delta \bar{S}_1, \Delta \bar{S}_1^E$ $\pm$ 0.3 cals/deg/mole, |
| $\Delta H_1$ $\pm$ 160 cals/mole, | $\Delta \bar{H}_1$ $\pm$ 250 cals/mole. |

Because of the inherent errors in the data obtained from graphical integration, the errors in both $\Delta G$ and $\Delta H$ will be much greater than

for the corresponding partial quantities for $PbBr_2$. This is especially true in the case of $\Delta H$, where the absolute error is in excess of 350 cals/mole and care must be taken in the interpretation of the position and magnitude of the maximum. As the quantities $\Delta\bar{G}_2$ and $\Delta\bar{H}_2$ are derived from both the integral and the partial functions of component 1, the errors associated with them will be of the same order of magnitude as for the integral quantities.

c) The system $PbBr_2$-RbBr

The e.m.f. variation of the formation cells with temperature, for each of seven mixtures, is represented in Table 3.9 and the equations to the lines of best fit, together with the mean deviation of the experimental points, are found in Table 3.10. These equations are plotted in fig. 3.8 and the e.m.f. isotherms are shown in fig. 3.9.

Activities and activity coefficients for $PbBr_2$ are listed in Table 3.11 and the values for RbBr, calculated from the graphical integration of the Gibbs-Duhem equation, are found in Table 3.12. Results are plotted in fig. 3.10. Partial integral and excess thermodynamic quantities for both components, are found in Tables 3.13 and 3.14 and these are plotted in figs. 3.11-3.13. The values for the quantities $\Delta\bar{G}_2$ and $\Delta\bar{H}_2$, listed in Table 3.14, were obtained at integral mole fractions of $PbBr_2$ by interpolation from the plots of $\Delta\bar{G}_1$ and $\Delta G$ vs. $N_1$ and $\Delta\bar{H}_1$ and $\Delta H$ vs. $N_1$ respectively. The uncertainty in this procedure is far less than the inaccuracies due to graphical integration.

The errors in both the activities and the other thermodynamic quantities are of the same order of magnitude as for the system $PbBr_2$-KBr.

d) The system $PbBr_2$-CsBr

The e.m.f. of the formation cells with $PbBr_2$ + CsBr as electrolyte, are summarized in Table 3.15 together with the e.m.f. deviation from the line of best fit. The equations for the lines and the mean deviations of the experimental points are represented in Table 3.16. These equations are plotted in fig. 3.14 and the e.m.f. isotherms are illustrated in fig. 3.15.

Activities and activity coefficients of $PbBr_2$ are summarized in Table 3.17 and the corresponding values for CsBr are found in Table 3.18. The quantities for both components are plotted in fig. 3.16. Partial, integral and excess thermodynamic quantities for $PbBr_2$ and CsBr, are listed in Tables 3.19 and 3.20 and are graphically presented in figs. 3.17-3.19. Tabulated values for $\Delta\bar{G}_2$ and $\Delta\bar{H}_2$ are obtained in a similar manner to the systems $PbBr_2$-RbBr and $PbBr_2$-KBr.

The magnitudes of the errors in this system are similar to those in the two preceding systems.

TABLE 3.1

Values of e.m.f. and temperature for the cell Pb/pure $PbBr_2$/C, $Br_2$

| temperature (°C) | e.m.f. (volts) | △E* (millivolts) | temperature (°C) | e.m.f. (volts) | △E* (millivolts) |
|---|---|---|---|---|---|
| 461.6 | 1.0375 | -0.3 | 601.2 | 0.9648 | +0.6 |
| 493.0 | 1.0213 | +0.1 | 635.0 | 0.9463 | 0.0 |
| 520.4 | 1.0064 | -0.4 | 667.2 | 0.9297 | +0.3 |
| 548.0 | 0.9923 | +0.1 | 699.5 | 0.9121 | -0.2 |
| 575.8 | 0.9776 | 0.0 | 727.1 | 0.8977 | -0.1 |

* △E refers to the deviation of the experimental points from the line of best fit.

TABLE 3.2

Thermodynamic properties of pure $PbBr_2$

| temperature (°C) | △G° (K cal/mole) | △S° (cal/deg/mole) | △H° (K cal/mole) |
|---|---|---|---|
| 500 | -46.93 | | |
| 600 | -44.50 | -24.33 | -65.74 |
| 700 | -42.07 | | |

## TABLE 3.3

### Values of e.m.f. and temperature for the formation cells: $Pb/PbBr_2(N_1) + KBr(N_2)/C, Br_2$

| composition (m.f.PbBr2) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) |
|---|---|---|---|---|---|---|
| 0.801 | 413.6 | 1.0755 | +0.4 | 560.1 | 0.9962 | 0.0 |
| | 440.7 | 1.0606 | +0.1 | 583.6 | 0.9839 | +0.4 |
| | 471.6 | 1.0437 | -0.2 | 648.0 | 0.9480 | -0.8 |
| | 500.2 | 1.0284 | 0.0 | 693.8 | 0.9241 | 0.0 |
| | 520.6 | 1.0170 | -0.4 | 736.0 | 0.9020 | +0.7 |
| 0.595 | 431.2 | 1.0822 | -0.2 | 602.8 | 0.9888 | 0.0 |
| | 486.8 | 1.0522 | +0.1 | 670.1 | 0.9522 | +0.1 |
| | 542.2 | 1.0221 | +0.3 | 732.7 | 0.9178 | -0.1 |
| | 573.5 | 1.0048 | 0.0 | | | |
| 0.503 | 431.4 | 1.1080 | +1.3 | 547.2 | 1.0425 | +0.2 |
| | 460.9 | 1.0903 | 0.0 | 596.6 | 1.0143 | -0.5 |
| | 488.2 | 1.0752 | +0.1 | 661.0 | 0.9791 | +0.2 |
| | 510.3 | 1.0627 | -0.1 | 725.0 | 0.9448 | +1.5 |
| 0.395 | 492.0 | 1.0135 | +0.8 | 630.2 | 1.0300 | 0.0 |
| | 547.4 | 1.0735 | -0.1 | 661.0 | 1.0130 | -0.8 |
| | 569.0 | 1.0622 | 0.0 | 732.4 | 0.9765 | +0.3 |
| | 599.4 | 1.0462 | 0.0 | | | |
| 0.197 | 648.2 | 1.0635 | +0.6 | 760.0 | 1.0209 | 0.0 |
| | 673.9 | 1.0532 | 0.0 | 788.0 | 1.0105 | +0.2 |
| | 691.2 | 1.0466 | -0.1 | 829.0 | 0.9955 | +0.5 |
| | 737.9 | 1.0293 | +0.1 | 876.0 | 0.9768 | -0.5 |

TABLE 3.4

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells: $Pb/PbBr_2(N_1) + KBr(N_2)/C, Br_2$

| composition (m.f.$PbBr_2$) | e.m.f. at temperature t°C (volts) | mean deviation of exptl. pts. from line (mv.) |
|---|---|---|
| 0.801 | $1.2981 - (5.391 \times 10^{-4})t$ | 0.3 |
| 0.595 | $1.3176 - (5.455 \times 10^{-4})t$ | 0.1 |
| 0.503 | $1.3469 - (5.567 \times 10^{-4})t$ | 0.2 |
| 0.395 | $1.3616 - (5.262 \times 10^{-4})t$ | 0.3 |
| 0.197 | $1.3064 - (3.757 \times 10^{-4})t$ | 0.3 |

TABLE 3.5

Value of the activity and activity coefficient of $PbBr_2$ at different compositions in the system $PbBr_2$-KBr

| composition (m.f.$PbBr_2$) | Activity $PbBr_2$ | | | Activity coeff. $PbBr_2$ | | |
|---|---|---|---|---|---|---|
| | 500°C | 600°C | 700°C | 500°C | 600°C | 700°C |
| 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 0.801 | 0.7190 | 0.7707 | 0.8127 | 0.8979 | 0.9625 | 1.0149 |
| 0.595 | 0.4409 | 0.5079 | 0.5684 | 0.7408 | 0.8535 | 0.9550 |
| 0.503 | 0.2165 | 0.2787 | 0.3406 | 0.4302 | 0.5538 | 0.6769 |
| 0.395 | 0.0881 | 0.1160 | 0.1440 | 0.2233 | 0.2941 | 0.3650 |
| 0.197 | 0.0483 | 0.0456 | 0.0437 | 0.2454 | 0.2317 | 0.2221 |

TABLE 3.6

Value of the activity and activity coefficient of KBr (600°C) at various compositions in the system $PbBr_2$-KBr

| composition (m.f. KBr) | activity KBr (600°C) | activity coefficient KBr (600°C) |
|---|---|---|
| 0.200 | 0.0386 | 0.1932 |
| 0.250 | 0.0507 | 0.2026 |
| 0.333 | 0.0730 | 0.2192 |
| 0.400 | 0.0931 | 0.2327 |
| 0.500 | 0.1374 | 0.2748 |
| 0.571 | 0.1929 | 0.3378 |
| 0.667 | 0.3064 | 0.4594 |
| 0.800 | 0.5257 | 0.6570 |
| 1.000 | 1.000 | 1.000 |

TABLE 3.7

Partial molar thermodynamic functions of $PbBr_2$ in the system $PbBr_2$-KBr

| | 600°C | | | | | |
|---|---|---|---|---|---|---|
| mole fraction $PbBr_2$ | 1.00 | 0.801 | 0.595 | 0.503 | 0.395 | 0.197 |
| $\triangle G_1$ (K cal/mole) | -44.50 | -44.95 | -45.68 | -46.72 | -48.24 | -49.86 |
| $\triangle S_1$ (cal/deg/mole) | -24.33 | -24.87 | -25.16 | -25.68 | -24.27 | -17.33 |
| $\triangle H_1$ (K cal/mole) | -65.74 | -66.66 | -67.64 | -69.14 | -69.43 | -64.99 |
| $\triangle \bar{G}_1$ (K cal/mole) | | - 0.45 | - 1.18 | - 2.22 | - 3.74 | - 5.36 |
| $\triangle \bar{S}_1$ (cal/deg/mole) | | - 0.54 | - 0.83 | - 1.35 | + 0.06 | + 0.70 |
| $\triangle \bar{H}_1$ (K cal/mole) | | - 0.92 | - 1.90 | - 3.39 | - 3.69 | + 0.75 |
| $\triangle \bar{G}_1^E$ (K cal/mole) | | - 0.04 | - 0.27 | - 1.03 | - 2.12 | - 2.54 |
| $\triangle \bar{S}_1^E$ (cal/deg/mole) | | - 0.98 | - 1.86 | - 2.71 | - 1.79 | + 4.55 |

Table 3.7 (contd.)

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | 500°C | | | |
| mole fraction $PbBr_2$ | 1.00 | 0.801 | 0.595 | 0.503 | 0.395 | 0.197 |
| $\Delta G_1$ (K cal/mole) | -46.93 | -47.44 | -48.19 | -49.28 | -50.67 | -51.59 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.51 | - 1.26 | - 2.35 | - 3.74 | - 4.66 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.17 | - 0.46 | - 1.30 | - 2.30 | - 2.16 |
| | | | 700°C | | | |
| $\Delta G_1$ (K cal/mole) | -42.07 | -42.47 | -43.16 | -44.15 | -45.82 | -48.13 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.40 | - 1.09 | - 2.09 | - 3.75 | - 6.06 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | + 0.03 | - 0.09 | - 0.75 | - 1.95 | - 2.91 |

TABLE 3.8

Integral thermodynamic functions for the system $PbBr_2$-KBr and partial molar thermodynamic functions for KBr at 600°C

| | | | | | |
|---|---|---|---|---|---|
| mole fraction $PbBr_2$ | 1.00 | 0.90 | 0.80 | 0.70 | 0.60 |
| $\Delta G$ (K cal/mole) | 0 | -0.92 | -1.63 | -2.17 | -2.54 |
| $\Delta \bar{G}_2$ (K cal/mole) | | -8.10 | -6.35 | -5.30 | -4.55 |
| $\Delta H$ (K cal/mole) | 0 | -0.99 | -1.35 | -1.44 | -1.36 |
| $\Delta \bar{H}_2$ (K cal/mole) | | -5.20 | -3.05 | -1.60 | -0.60 |
| mole fraction $PbBr_2$ | 0.50 | 0.40 | 0.30 | 0.20 | 0.10 |
| $\Delta G$ (K cal/mole) | -2.76 | -2.73 | -2.48 | -2.10 | -1.46 |
| $\Delta \bar{G}_2$ (K cal/mole) | -3.18 | -2.05 | -1.56 | -1.29 | - |
| $\Delta H$ (K cal/mole) | -1.05 | -0.52 | -0.04 | +0.09 | +0.02 |
| $\Delta \bar{H}_2$ (K cal/mole) | +1.30 | +1.58 | +0.54 | -0.04 | - |

TABLE 3.9

Values of e.m.f. and temperature for the formation cells:
$Pb/PbBr_2(N_1) + RbBr(N_2)/C, Br_2$

| composition (m.f.$PbBr_2$) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) |
|---|---|---|---|---|---|---|
| 0.872 | 505.2 | 1.0204 | -0.3 | 607.0 | 0.9670 | 0 |
| | 531.4 | 1.0068 | -0.1 | 628.3 | 0.9558 | 0 |
| | 556.5 | 0.9940 | +0.4 | 657.1 | 0.9405 | -0.1 |
| | 581.8 | 0.9804 | +0.1 | | | |
| 0.799 | 511.8 | 1.0221 | -0.5 | 615.4 | 0.9686 | -0.1 |
| | 542.0 | 1.0069 | 0 | 640.3 | 0.9558 | 0 |
| | 567.0 | 0.9941 | +0.2 | 669.9 | 0.9403 | -0.1 |
| | 593.0 | 0.9809 | +0.5 | | | |
| 0.696 | 515.1 | 1.0295 | -0.4 | 619.8 | 0.9754 | -0.3 |
| | 541.8 | 1.0158 | -0.3 | 647.3 | 0.9617 | +0.2 |
| | 568.0 | 1.0032 | +0.7 | 677.1 | 0.9461 | 0 |
| | 593.2 | 0.9896 | +0.1 | | | |
| 0.600 | 521.6 | 1.0396 | -0.8 | 627.4 | 0.9875 | +0.1 |
| | 548.3 | 1.0268 | -0.3 | 651.2 | 0.9755 | 0 |
| | 574.6 | 1.0145 | +0.6 | 679.3 | 0.9614 | 0 |
| | 601.2 | 1.0011 | +0.5 | | | |
| 0.497 | 519.0 | 1.0654 | -0.1 | 628.0 | 1.0121 | +0.2 |
| | 546.0 | 1.0518 | -0.4 | 656.1 | 0.9979 | -0.2 |
| | 573.2 | 1.0389 | 0 | 685.9 | 0.9836 | +0.2 |
| | 600.0 | 1.0259 | +0.2 | | | |
| 0.400 | 525.0 | 1.0869 | -0.4 | 633.2 | 1.0359 | +0.1 |
| | 554.0 | 1.0733 | -0.2 | 660.1 | 1.0230 | 0 |
| | 581.8 | 1.0605 | +0.2 | 687.3 | 1.0102 | +0.1 |
| | 607.2 | 1.0482 | 0 | | | |
| 0.302 | 548.6 | 1.1031 | -0.2 | 654.4 | 1.0567 | +0.4 |
| | 575.0 | 1.0912 | -0.4 | 679.3 | 1.0453 | 0 |
| | 601.2 | 1.0800 | 0 | 703.7 | 1.0345 | +0.1 |
| | 627.0 | 1.0687 | +0.2 | | | |

TABLE 3.10

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells of the system $PbBr_2$-RbBr

| composition (m.f.$PbBr_2$) | e.m.f. at temperature t°C (volts) | mean deviation of exptl. pts. from line (mv.) |
|---|---|---|
| 0.872 | $1.2872 - (5.275 \times 10^{-4})t$ | 0.2 |
| 0.799 | $1.2888 - (5.202 \times 10^{-4})t$ | 0.2 |
| 0.696 | $1.2966 - (5.177 \times 10^{-4})t$ | 0.3 |
| 0.600 | $1.3017 - (5.009 \times 10^{-4})t$ | 0.3 |
| 0.497 | $1.3207 - (4.917 \times 10^{-4})t$ | 0.2 |
| 0.400 | $1.3369 - (4.755 \times 10^{-4})t$ | 0.1 |
| 0.302 | $1.3472 - (4.445 \times 10^{-4})t$ | 0.2 |

TABLE 3.11

Value of the activity and activity coefficient of $PbBr_2$ at different compositions in the system $PbBr_2$-RbBr

| composition (m.f.$PbBr_2$) | Activity $PbBr_2$ | | | Activity coeff. $PbBr_2$ | | |
|---|---|---|---|---|---|---|
| | 500°C | 600°C | 700°C | 500°C | 600°C | 700°C |
| 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 0.872 | 0.8377 | 0.8549 | 0.8688 | 0.9610 | 0.9811 | 0.9967 |
| 0.799 | 0.7147 | 0.7290 | 0.7389 | 0.8943 | 0.9122 | 0.9245 |
| 0.696 | 0.5455 | 0.5696 | 0.5891 | 0.7835 | 0.8183 | 0.8462 |
| 0.600 | 0.3639 | 0.3802 | 0.3938 | 0.6064 | 0.6334 | 0.6562 |
| 0.497 | 0.1793 | 0.1985 | 0.2149 | 0.3606 | 0.3992 | 0.4322 |
| 0.400 | 0.0865 | 0.1000 | 0.1116 | 0.2161 | 0.2499 | 0.2789 |
| 0.302 | 0.0398 | 0.0462 | 0.0521 | 0.1318 | 0.1530 | 0.1726 |

TABLE 3.12

Value of the activity and activity coefficient of RbBr at various compositions and at 600°C in the system $PbBr_2$-RbBr

| composition (m.f. RbBr) | activity RbBr(600°C) | activity coefficient RbBr (600°C) |
|---|---|---|
| 0.128 | 0.0079 | 0.0614 |
| 0.167 | 0.0109 | 0.0650 |
| 0.200 | 0.0140 | 0.0702 |
| 0.250 | 0.0196 | 0.0783 |
| 0.308 | 0.0273 | 0.0885 |
| 0.364 | 0.0370 | 0.1017 |
| 0.444 | 0.0573 | 0.1290 |
| 0.500 | 0.0793 | 0.1585 |
| 0.571 | 0.1192 | 0.2087 |
| 0.667 | 0.2035 | 0.3052 |
| 0.800 | 0.4035 | 0.5044 |

TABLE 3.13

**Partial molar thermodynamic functions of $PbBr_2$ in the system $PbBr_2$-RbBr**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 600°C | | | |
| mole fraction $PbBr_2$ | 1.000 | 0.872 | 0.799 | 0.696 | 0.600 | 0.497 | 0.400 | 0.302 |
| $\Delta G_1$ (K cal/mole) | -44.50 | -44.77 | -45.05 | -45.48 | -46.18 | -47.31 | -48.50 | -49.84 |
| $\Delta S_1$ (cal/deg/mole) | -24.33 | -24.33 | -23.99 | -23.88 | -23.10 | -22.68 | -21.93 | -20.50 |
| $\Delta H_1$ (K cal/mole) | -65.74 | -66.01 | -65.99 | -66.33 | -66.35 | -67.11 | -67.65 | -67.73 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.27 | - 0.55 | - 0.98 | - 1.68 | - 2.81 | - 4.00 | - 5.34 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | 0 00 | + 0.34 | + 0.45 | + 1.23 | + 1.65 | + 2.40 | + 3.82 |
| $\Delta \bar{H}_1$ (K cal/mole) | | - 0.26 | - 0.25 | - 0.59 | - 0.61 | - 1.37 | - 1.91 | - 1.99 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.03 | - 0.16 | - 0/35 | - 0.79 | - 1.59 | - 2.41 | - 3.26 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | - 0.27 | - 0.11 | - 0.27 | + 0.21 | + 0.26 | + 0.58 | + 1.45 |
| | | | | | 500°C | | | |
| $\Delta G_1$ (K cal/mole) | -46.93 | -47.20 | -47.45 | -47.86 | -48.49 | -49.57 | -50.70 | -51.89 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.27 | - 0.52 | - 0.93 | - 1.56 | - 2.64 | - 3.76 | - 4.95 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.06 | - 0.17 | - 0.38 | - 0.77 | - 1.57 | - 2.35 | - 3.12 |
| | | | | | 700°C | | | |
| $\Delta G_1$ (K cal/mole) | -42.07 | -42.34 | -42.65 | -43.09 | -43.87 | -45.04 | -46.31 | -47.78 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.27 | - 0.57 | - 1.02 | - 1.80 | - 2.98 | - 4.24 | - 5.72 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.01 | - 0.15 | - 0.32 | - 0.82 | - 1.62 | - 2.47 | - 3.40 |

TABLE 3.14

Integral thermodynamic functions for the system $PbBr_2$-RbBr and partial molar thermodynamic functions for RbBr at 600°C

| mole fraction $PbBr_2$ | 1.0 | 0.90 | 0.80 | 0.70 | 0.60 |
|---|---|---|---|---|---|
| $\Delta G$ (K cal/mole) | 0.0 | -1.18 | -2.06 | -2.76 | -3.22 |
| $\Delta \bar{G}_2$ (K cal/mole) | - | -10.30 | -8.10 | -6.77 | -5.55 |
| $\Delta H$ (K cal/mole) | 0.0 | -0.43 | -0.61 | -0.74 | -0.81 |
| $\Delta \bar{H}_2$ (K cal/mole) | - | -2.18 | -0.62 | -1.08 | -1.10 |
| mole fractipn $PbBr_2$ | 0.50 | 0.40 | 0.30 | 0.20 | 0.10 |
| $\Delta G$ (K cal/mole) | -3.49 | -3.51 | -3.32 | -2.90 | -2.09 |
| $\Delta \bar{G}_2$ (K cal/mole) | -4.24 | -3.18 | -2.43 | - | - |
| $\Delta H$ (K cal/mole) | -0.79 | -0.62 | -0.40 | -0.20 | -0.05 |
| $\Delta \bar{H}_2$ (K cal/mole) | -0.24 | +0.24 | +0.28 | - | - |

TABLE 3.15

Values of e.m.f. and temperature for the formation cells:
$Pb/PbBr_2(N_1) + CsBr(N_2)/C, Br_2$

| composition (m.f.$PbBr_2$) | temp. (°C) | e.m.f. (volts) | △E (mv.) | temp. (°C) | e.m.f. (volts) | △E (mv.) |
|---|---|---|---|---|---|---|
| 0.872 | 565.5 | 0.9853 | -0.4 | 672.6 | 0.9312 | -0.3 |
| | 595.0 | 0.9710 | +0.2 | 700.1 | 0.9179 | +0.3 |
| | 619.2 | 0.9587 | +0.2 | 727.9 | 0.9037 | +0.1 |
| | 645.8 | 0.9449 | -0.2 | | | |
| 0.794 | 582.0 | 0.9831 | +0.1 | 686.2 | 0.9310 | -0.9 |
| | 608.4 | 0.9702 | +0.1 | 710.7 | 0.9199 | 0.0 |
| | 634.0 | 0.9578 | +0.3 | 737.6 | 0.9068 | +0.1 |
| | 660.0 | 0.9450 | +0.3 | | | |
| 0.701 | 618.0 | 0.9777 | -0.3 | 722.6 | 0.9259 | -0.9 |
| | 644.0 | 0.9657 | +0.4 | 751.9 | 0.9125 | +0.1 |
| | 669.5 | 0.9534 | +0.6 | 777.6 | 0.9000 | +0.2 |
| | 696.7 | 0.9396 | +0.1 | | | |
| 0.629 | 613.0 | 0.9896 | -0.3 | 723.2 | 0.9378 | +0.3 |
| | 641.0 | 0.9768 | +0.2 | 751.3 | 0.9243 | +0.2 |
| | 668.0 | 0.9638 | +0.1 | 778.0 | 0.9112 | -0.2 |
| | 694.6 | 0.9509 | -0.2 | | | |
| 0.552 | 614.4 | 1.0023 | -0.1 | 719.8 | 0.9539 | -0.5 |
| | 642.0 | 0.9898 | -0.1 | 745.2 | 0.9426 | -0.3 |
| | 667.0 | 0.9792 | +0.7 | 771.7 | 0.9308 | 0.0 |
| | 693.2 | 0.9667 | +0.2 | | | |
| 0.451 | 613.2 | 1.0301 | +0.2 | 717.0 | 0.9840 | +0.6 |
| | 638.8 | 1.0182 | -0.2 | 745.5 | 0.9709 | +0.3 |
| | 662.8 | 1.0073 | -0.4 | 770.1 | 0.9597 | +0.1 |
| | 690.0 | 0.9952 | -0.3 | | | |
| 0.352 | 597.0 | 1.0777 | +0.1 | 699.0 | 1.0349 | 0.0 |
| | 623.0 | 1.0668 | +0.1 | 727.1 | 1.0231 | 0.0 |
| | 648.2 | 1.0563 | +0.1 | 755.7 | 1.0113 | +0.1 |
| | 673.2 | 1.0456 | -0.1 | | | |

TABLE 3.16

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells: $Pb/PbBr_2(N_1) + CsBr(N_2)/C, Br$

| composition (m.f.$PbBr_2$) | e.m.f. at temperature t°C (volts) | mean deviation of exptl. pts. from line (mv.) |
|---|---|---|
| 0.872 | $1.2718 - (5.059 \times 10^{-4})t$ | 0.3 |
| 0.794 | $1.2686 - (4.907 \times 10^{-4})t$ | 0.3 |
| 0.701 | $1.2807 - (4.898 \times 10^{-4})t$ | 0.4 |
| 0.629 | $1.2815 - (4.757 \times 10^{-4})t$ | 0.2 |
| 0.552 | $1.2823 - (4.555 \times 10^{-4})t$ | 0.3 |
| 0.451 | $1.3046 - (4.480 \times 10^{-4})t$ | 0.3 |
| 0.352 | $1.3275 - (4.186 \times 10^{-4})t$ | 0.1 |

TABLE 3.17

Value of the activity and activity coefficient of $PbBr_2$ at different compositions for the system $PbBr_2$-CsBr

| composition (m.f.$PbBr_2$) | Activity $PbBr_2$ | | | Activity coeff. $PbBr_2$ | | |
|---|---|---|---|---|---|---|
| | 500°C | 600°C | 700°C | 500°C | 600°C | 700°C |
| 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 0.872 | 0.9618 | 0.9111 | 0.8730 | 1.1034 | 1.0450 | 1.0015 |
| 0.794 | 0.8428 | 0.7791 | 0.7318 | 1.0613 | 0.9811 | 0.9215 |
| 0.701 | 0.5776 | 0.5575 | 0.5406 | 0.8242 | 0.7956 | 0.7714 |
| 0.629 | 0.4571 | 0.4354 | 0.4189 | 0.7269 | 0.6923 | 0.6662 |
| 0.552 | 0.3296 | 0.3091 | 0.2937 | 0.5976 | 0.5604 | 0.5325 |
| 0.451 | 0.1506 | 0.1516 | 0.1522 | 0.3341 | 0.3362 | 0.3376 |
| 0.352 | 0.0489 | 0.0518 | 0.0540 | 0.1389 | 0.1471 | 0.1534 |

TABLE 3.18

Value of the activity and activity coefficient of CsBr at various compositions and at 600°C for the system $PbBr_2$-CsBr

| composition (m.f. CsBr) | activity CsBr (600°C) | activity coefficient CsBr (600°C) |
|---|---|---|
| 0.182 | 0.0025 | 0.0137 |
| 0.222 | 0.0040 | 0.0178 |
| 0.286 | 0.0081 | 0.0284 |
| 0.333 | 0.0128 | 0.0384 |
| 0.400 | 0.0219 | 0.0548 |
| 0.444 | 0.0331 | 0.0745 |
| 0.541 | 0.0563 | 0.1040 |
| 0.645 | 0.1304 | 0.2021 |
| 0.800 | 0.3242 | 0.4052 |

TABLE 3.19

Partial molar thermodynamic functions of $PbBr_2$ in the system $PbBr_2$-CsBr

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 600°C | | | | |
| mole fraction $PbBr_2$ | 1.000 | 0.872 | 0.794 | 0.701 | 0.629 | 0.552 | 0.451 | 0.352 |
| $\Delta G_1$ (K cal/mole) | -44.50 | -44.66 | -44.93 | -45.52 | -45.94 | -46.54 | -47.78 | -49.64 |
| $\Delta S_1$ (cal/deg/mole) | -24.33 | -23.33 | -22.63 | -22.59 | -21.94 | -20.99 | -20.66 | -19.31 |
| $\Delta H_1$ (K cal/mole) | -65.74 | -65.04 | -64.69 | -65.24 | -65.10 | -64.88 | -65.81 | -66.50 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.16 | - 0.43 | - 1.02 | - 1.44 | - 2.04 | - 3.28 | - 5.14 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | + 1.00 | + 1.70 | + 1.74 | + 2.39 | + 3.34 | + 3.67 | + 5.02 |
| $\Delta \bar{H}_1$ (K cal/mole) | | + 0.71 | + 1.05 | + 0.50 | + 0.73 | + 0.86 | - 0.07 | - 0.76 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | + 0.08 | - 0.03 | - 0.04 | - 0.64 | - 1.01 | - 1.89 | - 3.33 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | + 0.72 | + 1.24 | + 1.03 | + 1.47 | + 2.16 | + 2.08 | + 2.95 |
| | | | | 500°C | | | | |
| $\Delta G_1$ (K cal/mole) | -46.93 | -46.99 | -47.19 | -47.78 | -48.14 | -48.64 | -49.84 | -51.58 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.06 | - 0.26 | - 0.84 | - 1.20 | - 1.71 | - 2.91 | - 4.65 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | + 0.15 | + 0.09 | - 0.30 | - 0.49 | - 0.79 | - 1.68 | - 3.03 |
| | | | | 700°C | | | | |
| $\Delta G_1$ (K cal/mole) | -42.07 | -42.33 | -42.67 | -43.26 | -43.75 | -44.44 | -45.71 | -47.72 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.26 | - 0.60 | - 1.19 | - 1.68 | - 2.37 | - 3.64 | - 5.65 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | 0.00 | - 0.16 | - 0.50 | - 0.79 | - 1.22 | - 2.10 | - 3.63 |

TABLE 3.20

**Integral thermodynamic functions for the system $PbBr_2$-CsBr and partial molar thermodynamic functions for CsBr at 600°C**

| mole fraction $PbBr_2$ | 1.0 | 0.90 | 0.80 | 0.70 | 0.60 |
|---|---|---|---|---|---|
| $\Delta G$ (K cal/mole) | 0.0 | - 1.22 | -2.28 | -3.09 | -3.70 |
| $\Delta \bar{G}_2$ (K cal/mole) | - | -11.90 | -9.70 | -7.93 | -6.80 |
| $\Delta H$ (K cal/mole) | 0.0 | + 0.45 | +0.38 | +0.13 | -0.06 |
| $\Delta \bar{H}_2$ (K cal/mole) | - | - | -2.29 | -0.75 | -1.32 |
| mole fraction $PbBr_2$ | 0.50 | 0.40 | 0.30 | 0.20 | 0.10 |
| $\Delta G$ (K cal/mole) | -4.12 | - 4.28 | -4.19 | -3.54 | -2.32 |
| $\Delta \bar{G}_2$ (K cal/mole) | -5.62 | - 4.47 | -3.19 | - | - |
| $\Delta H$ (K cal/mole) | -0.26 | -0.31 | -0.23 | -0.13 | -0.04 |
| $\Delta \bar{H}_2$ (K cal/mole) | -0.92 | -0.24 | - | - | - |

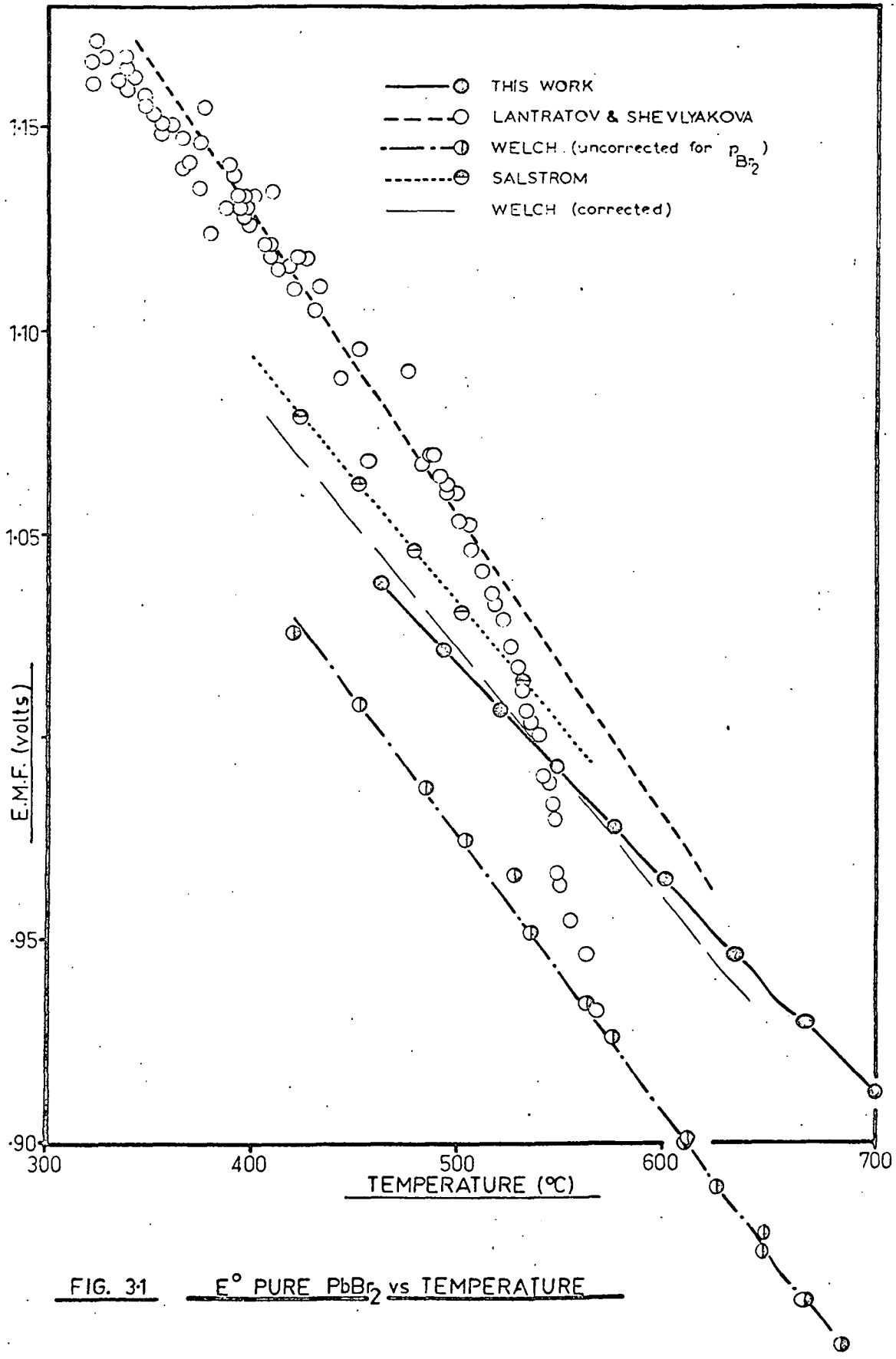



FIG. 3·1 E° PURE $PbBr_2$ vs TEMPERATURE

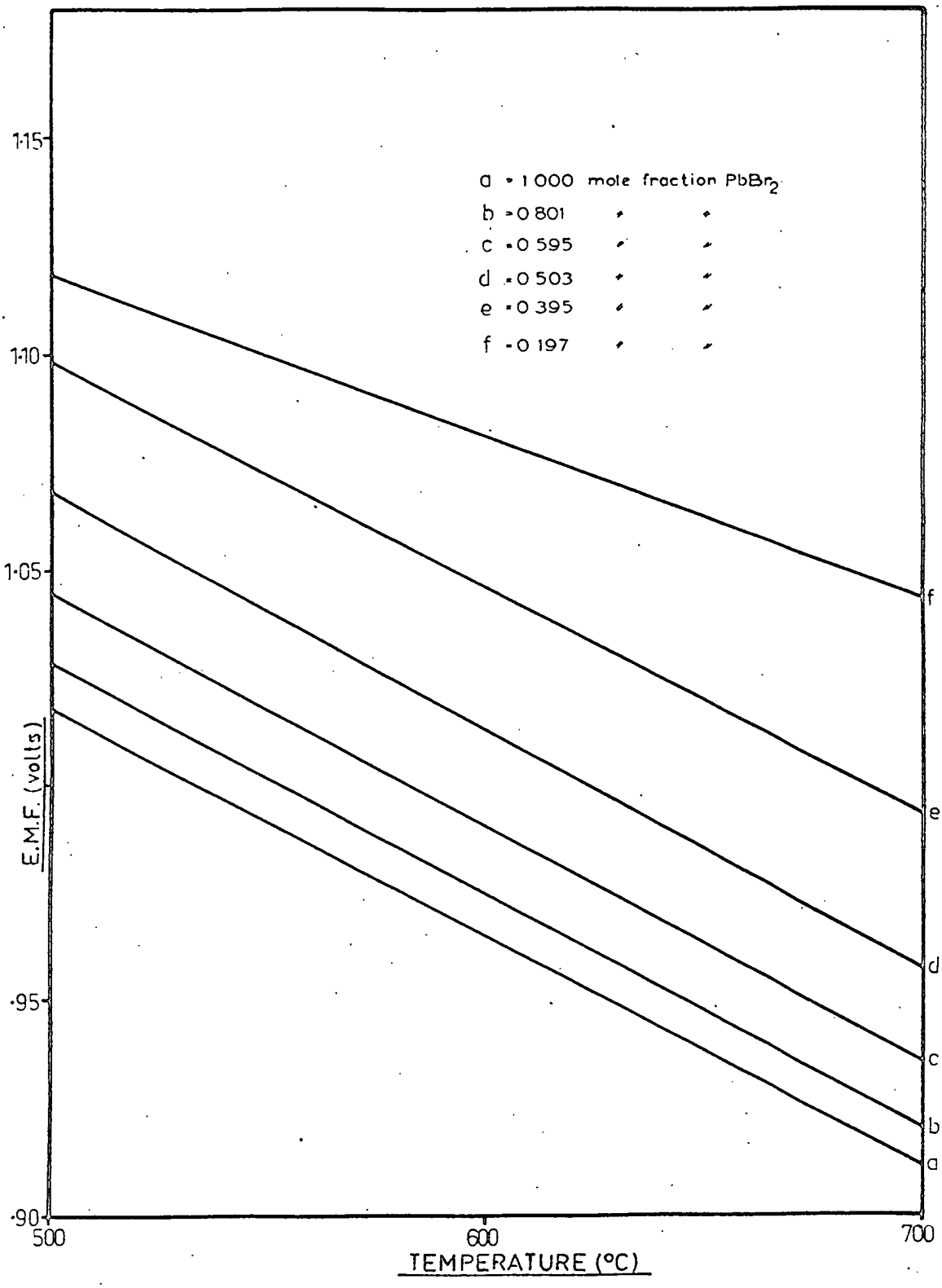



FIG. 3·2 SYSTEM $PbBr_2$-KBr
E.M.F. vs. TEMPERATURE

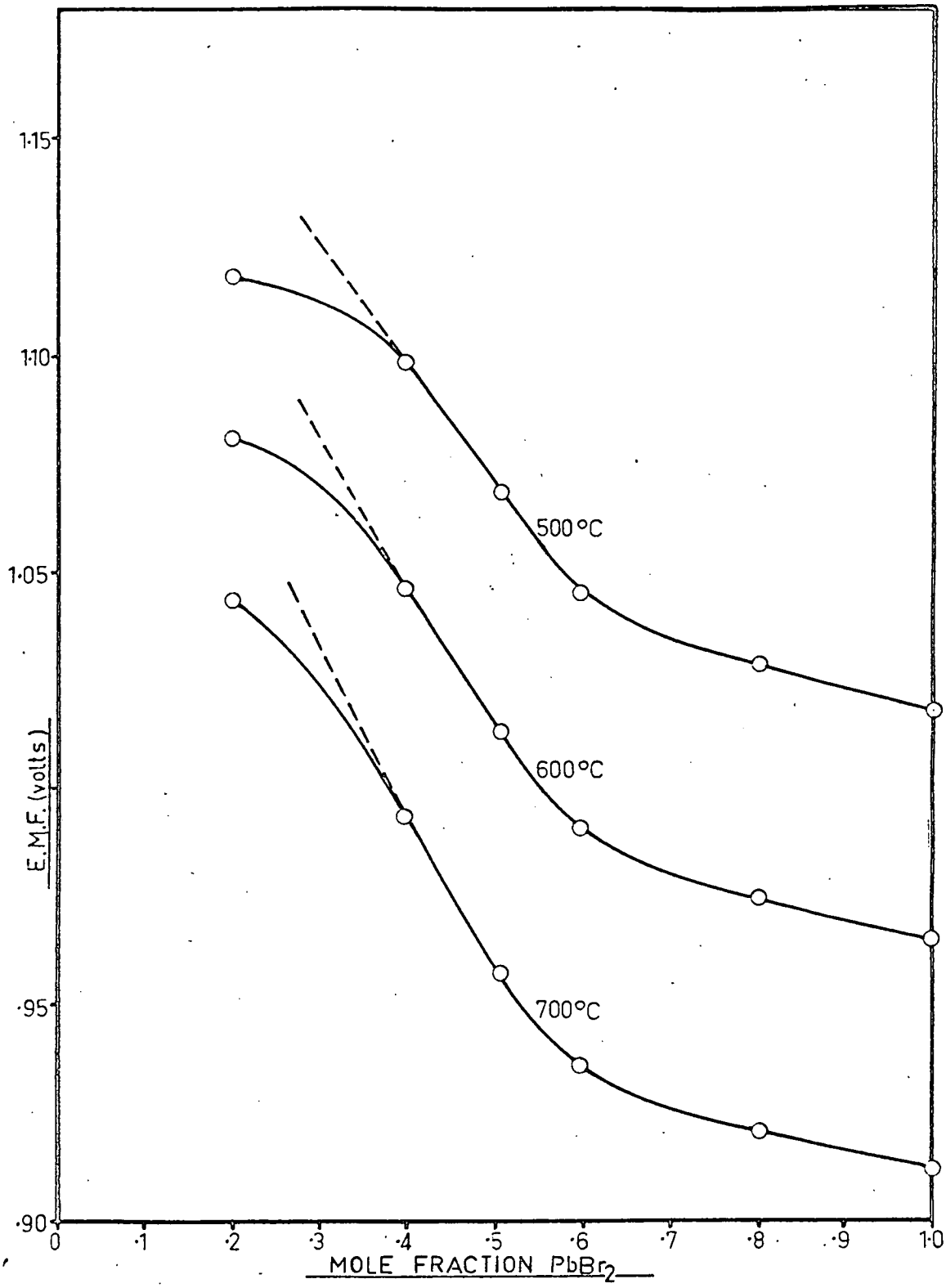



FIG. 33 SYSTEM $PbBr_2$ – KBr
E.M.F. vs COMPOSITION

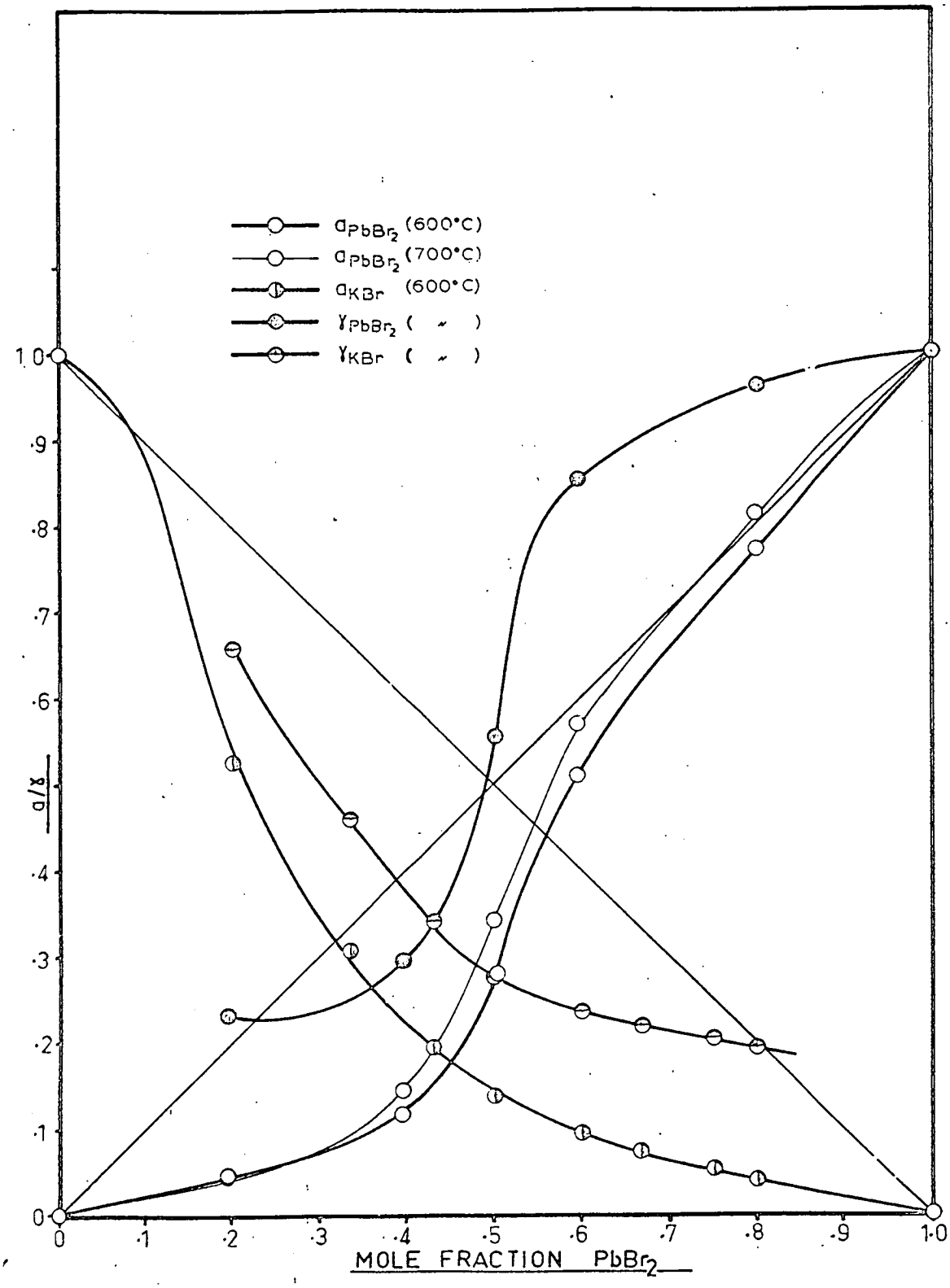



FIG. 3·4

SYSTEM $PbBr_2$–KBr

ACTIVITIES & ACTIVITY COEFFS. vs COMPOSITION

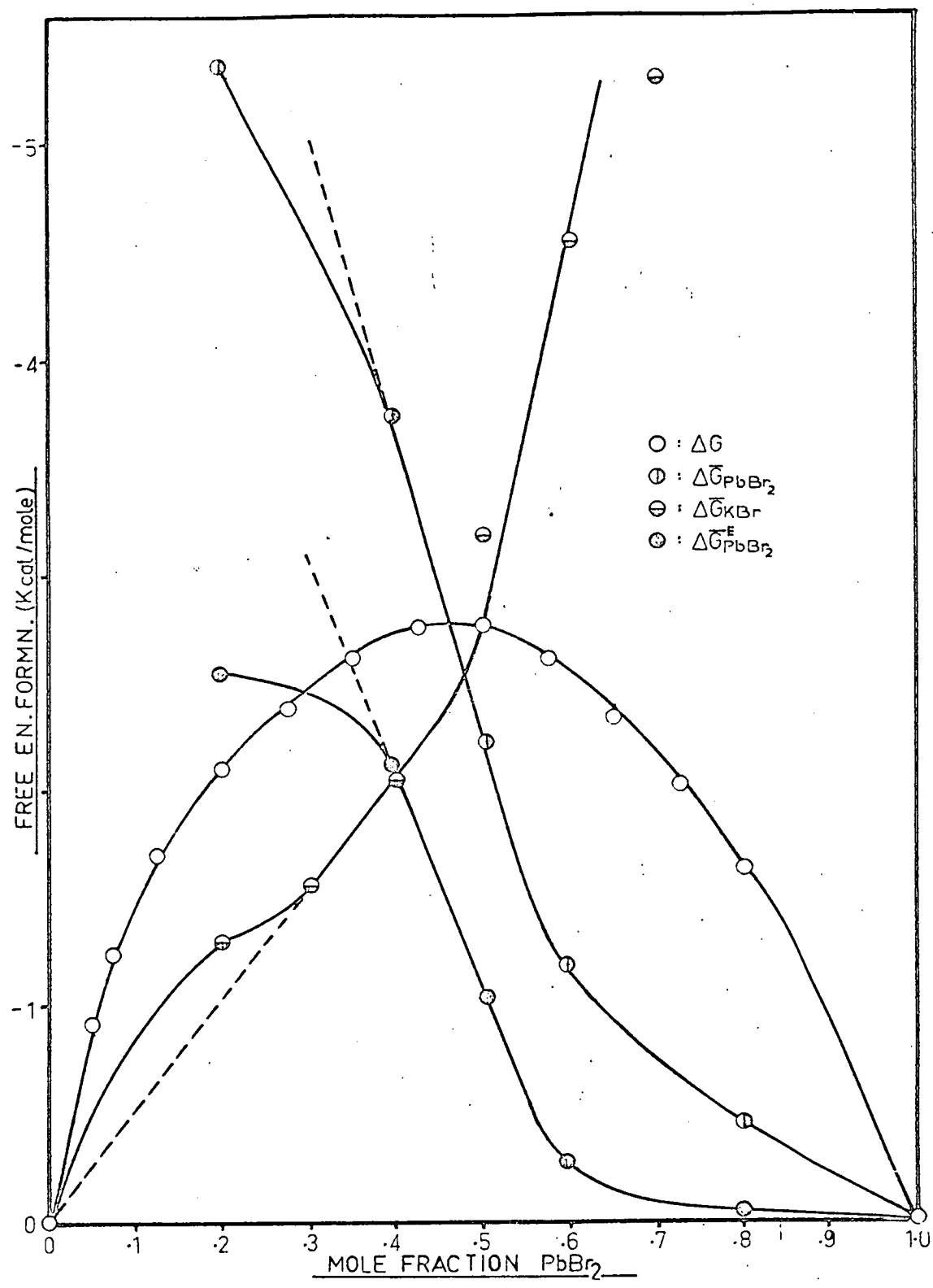



FIG. 3·5

SYSTEM $PbBr_2$–KBr (600°C)

PART., INTEG. & EXCESS FREE ENERGIES vs COMPOSITION

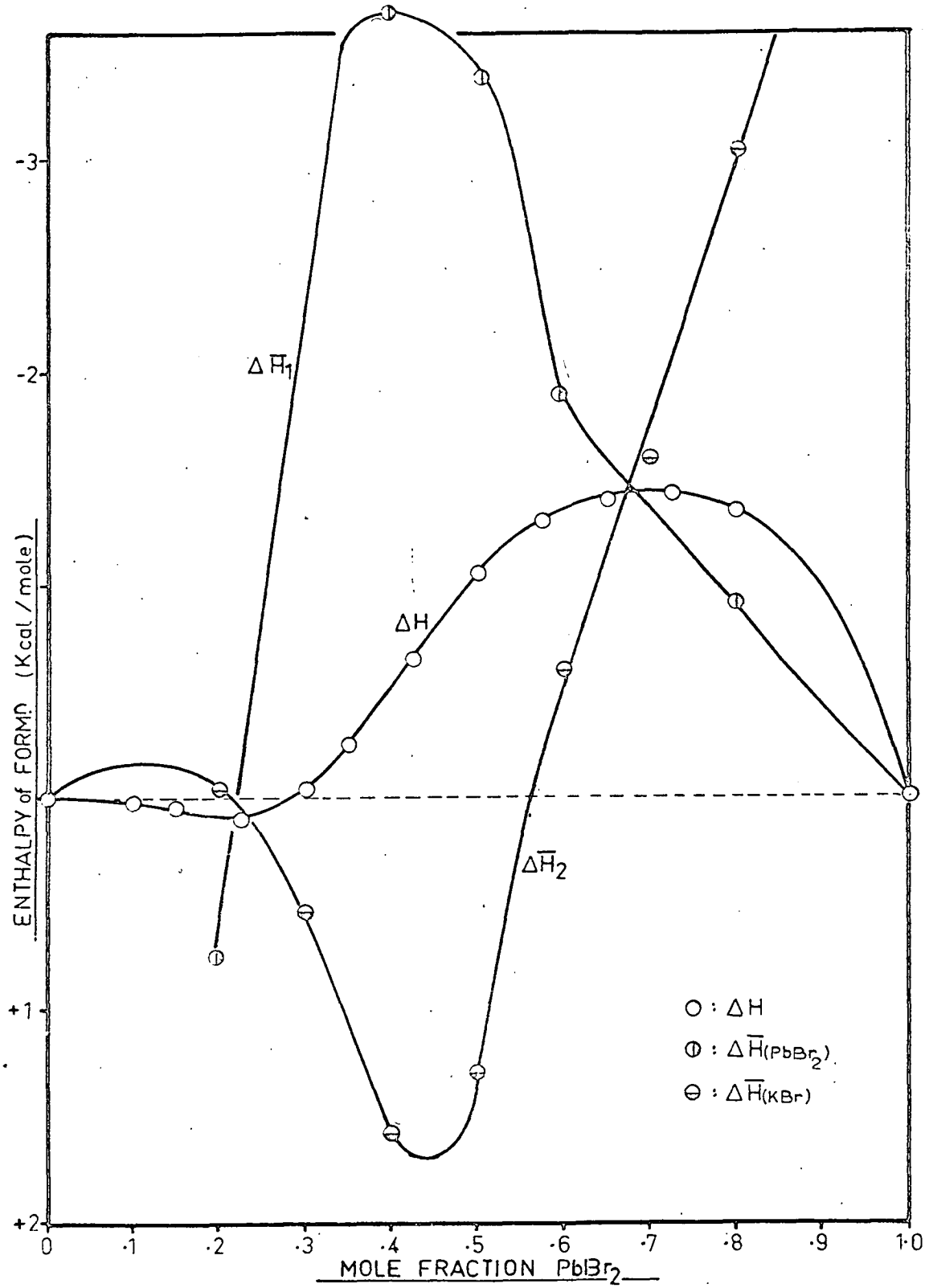



FIG. 3·6 SYSTEM $PbBr_2$—KBr

PARTIAL & INTEGRAL ENTHALPIES vs COMPOSITION

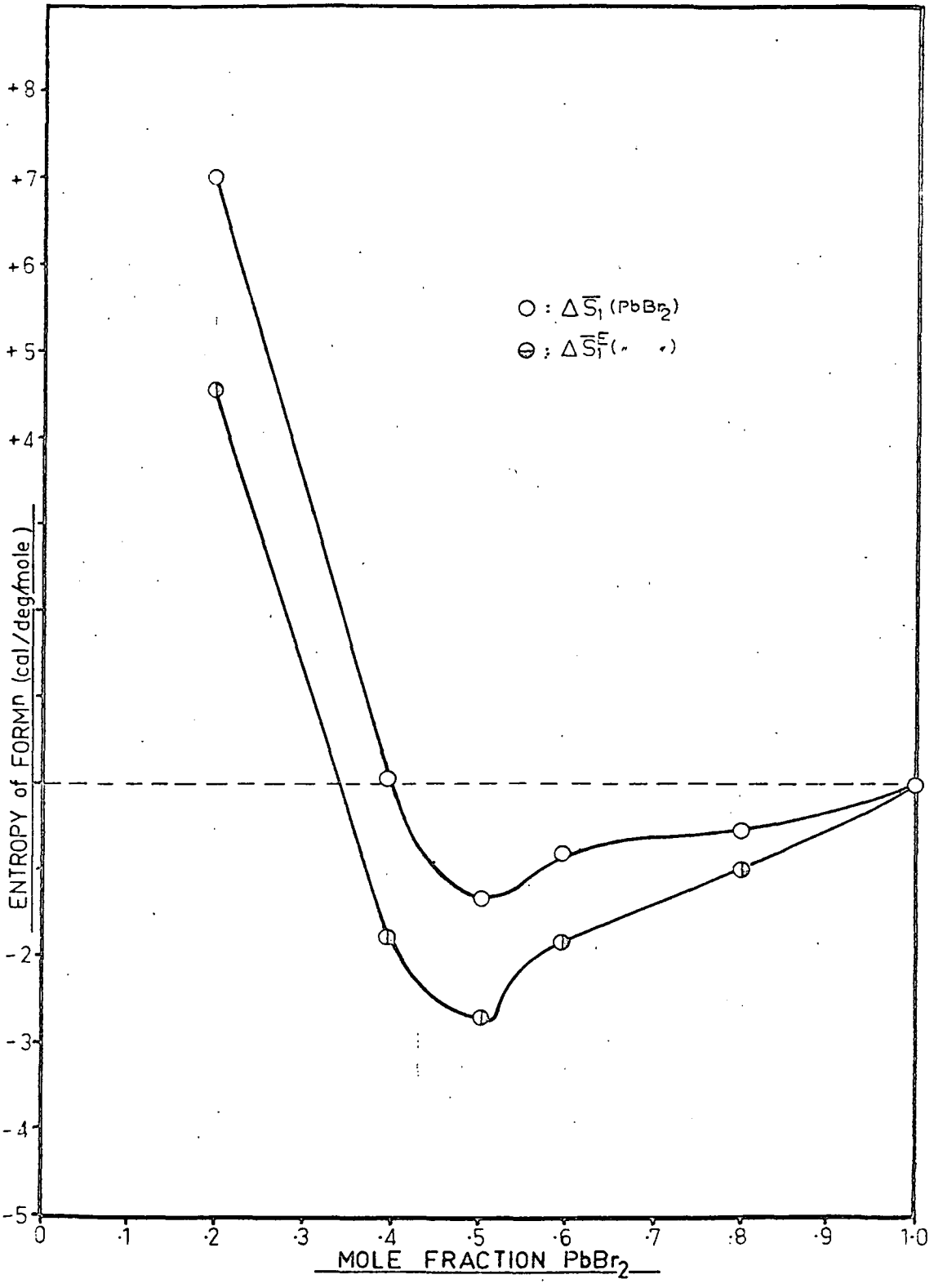



FIG. 3·7 SYSTEM $PbBr_2$–KBr

PARTIAL & EXCESS ENTROPY $PbBr_2$ vs COMPOSITION

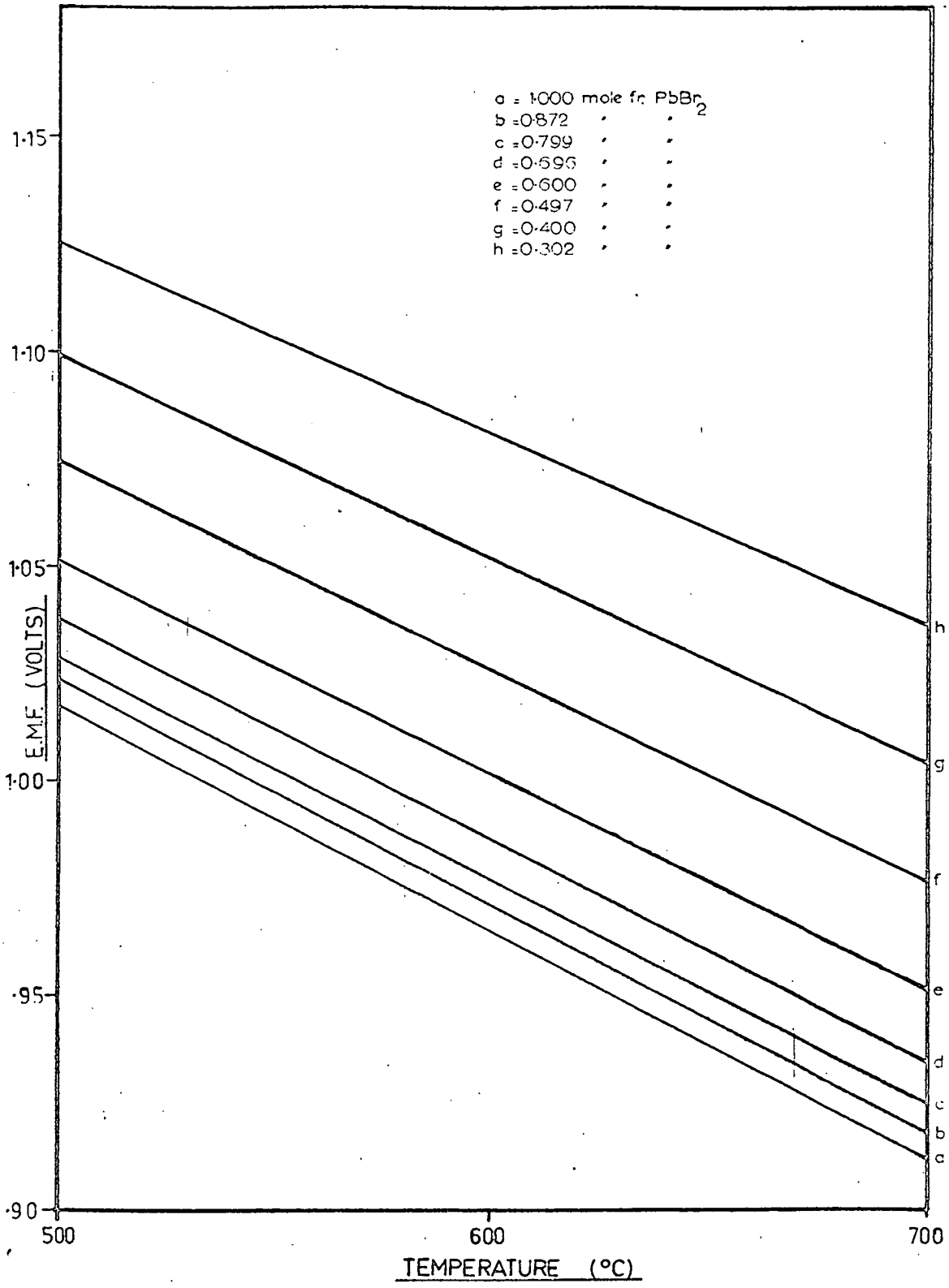



FIG. 3·8

SYSTEM $PbBr_2$-RbBr

E.M.F. vs. TEMPERATURE

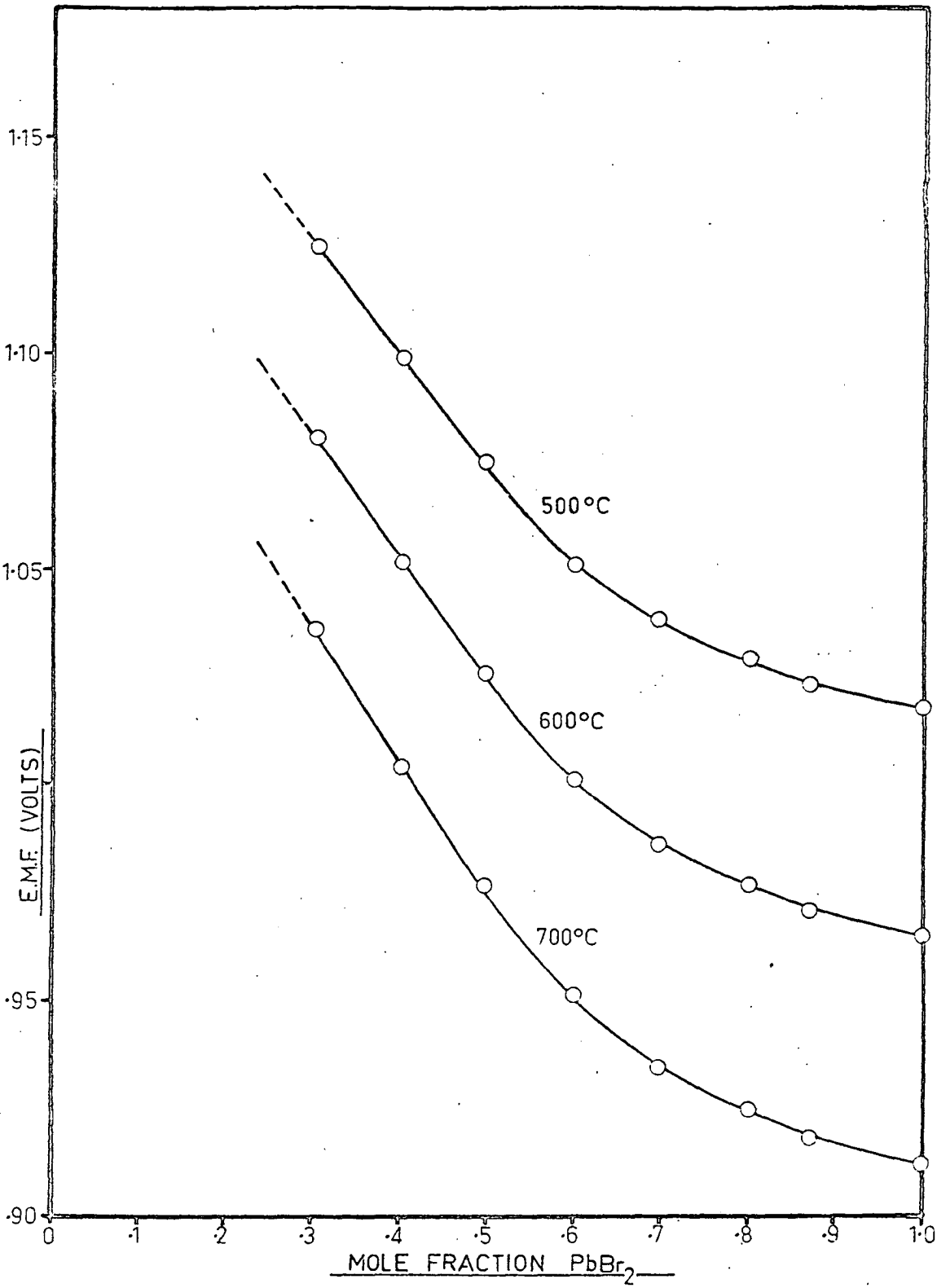



FIG. 3·9

SYSTEM $PbBr_2$ – RbBr

E.M.F. vs. COMPOSITION

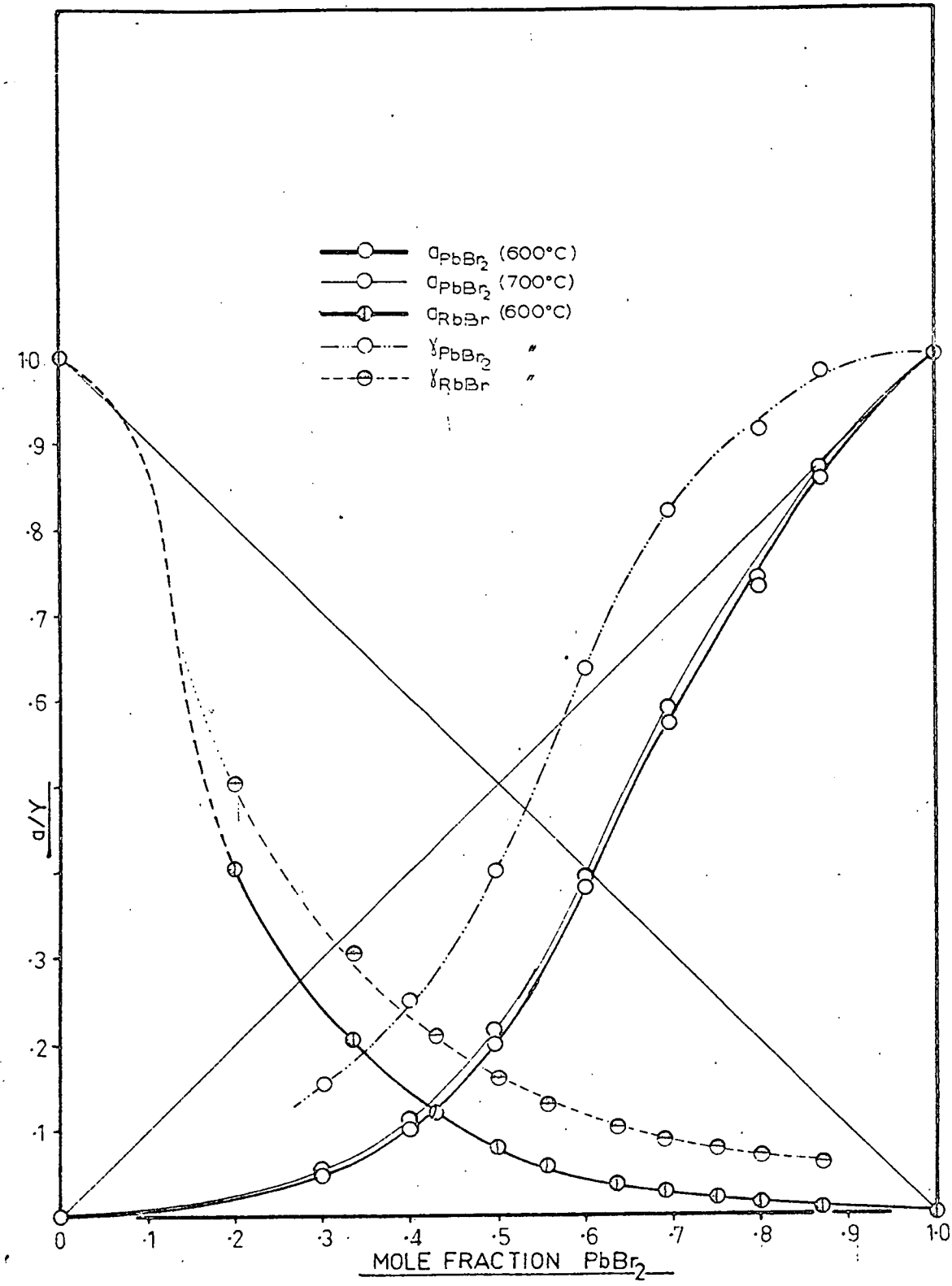



FIG. 3·10 SYSTEM $PbBr_2$-RbBr

ACTIVITIES & ACTIVITY COEFFS. vs. COMPOSITION

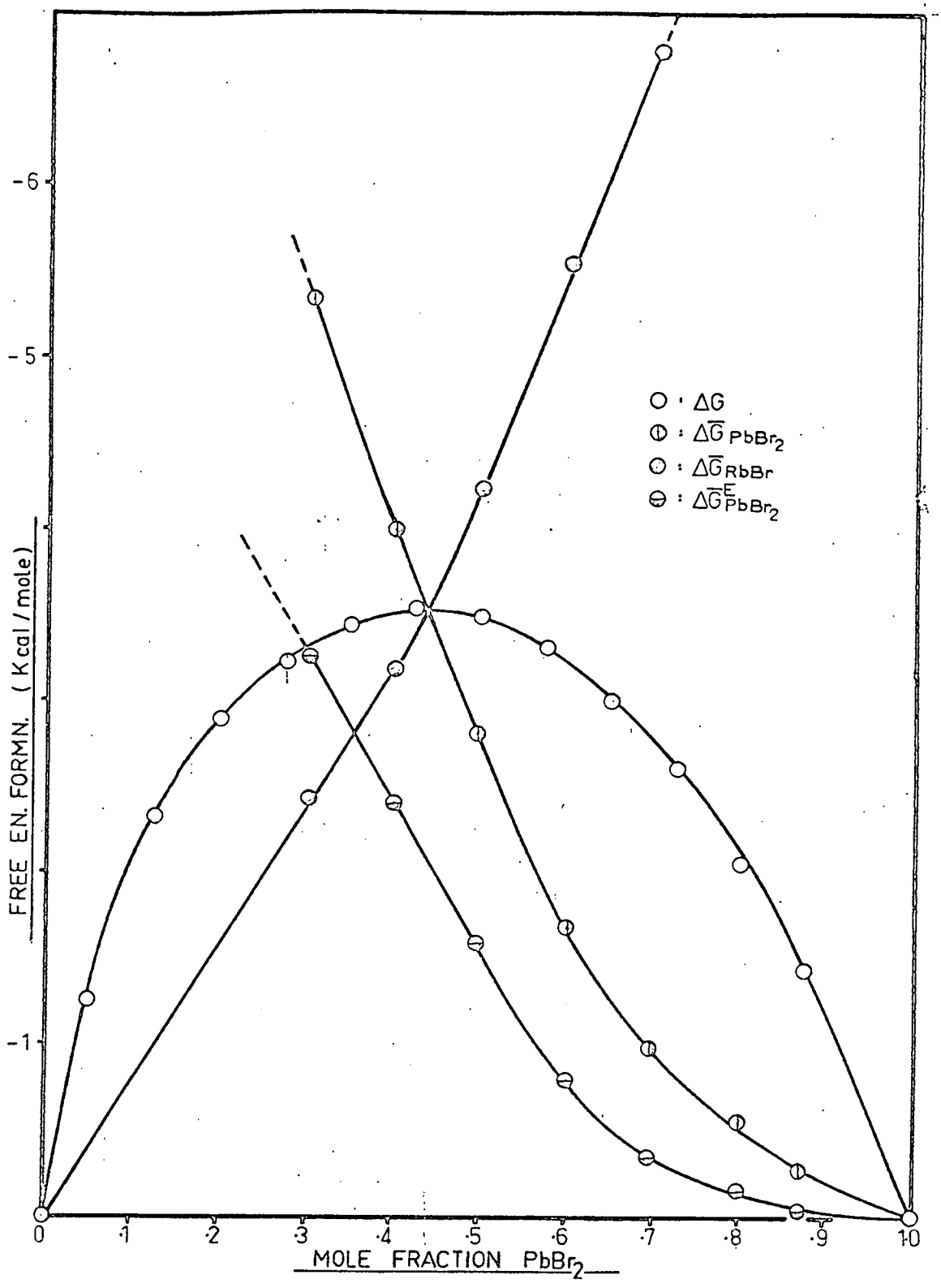



FIG. 3·11 SYSTEM $PbBr_2$–RbBr (600°C)
PART., INTEG. & EXCESS FREE ENERGIES vs COMPOSITION

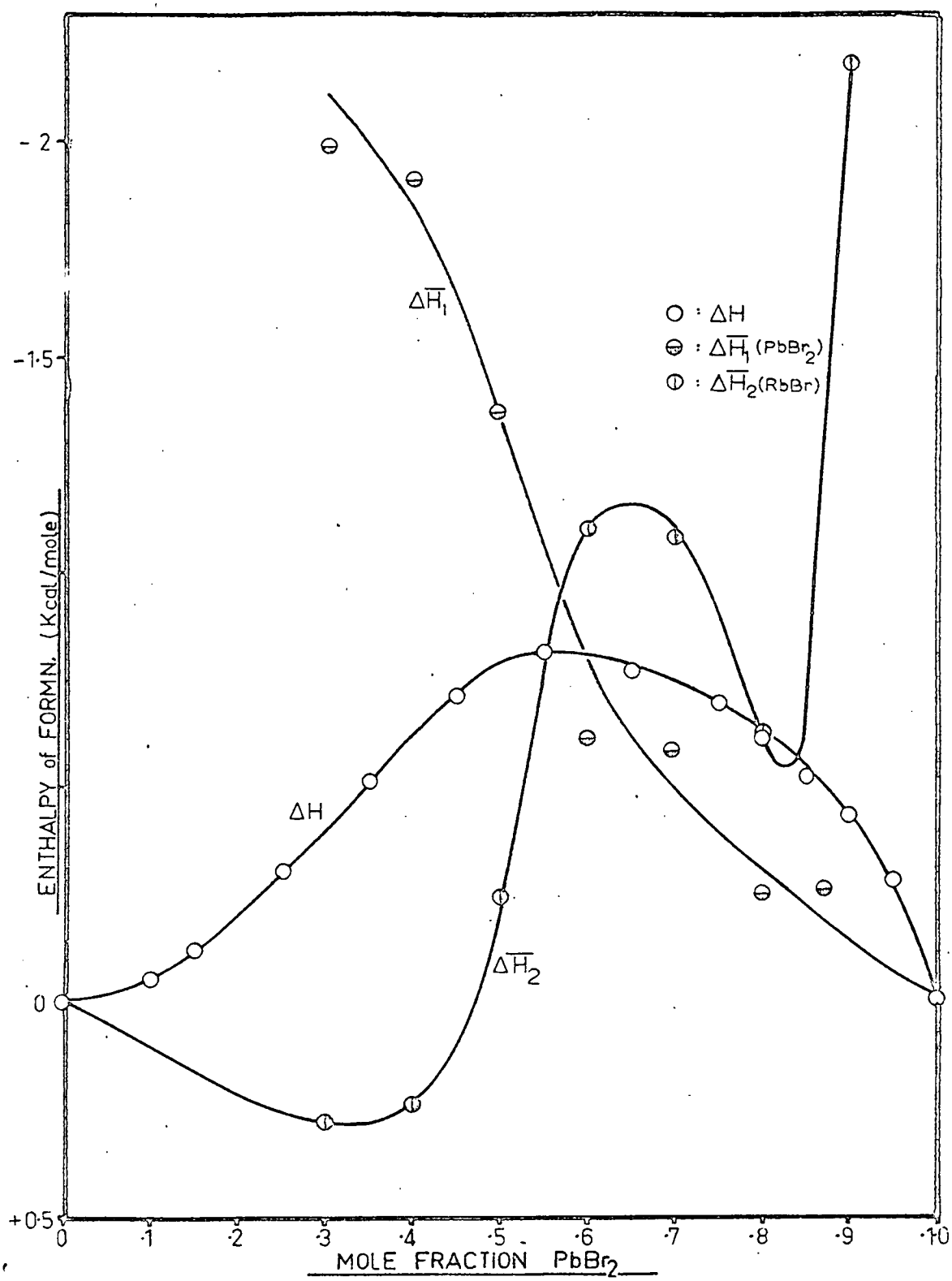



FIG. 3·12 SYSTEM $PbBr_2$–RbBr

PARTIAL & INTEGRAL ENTHALPIES vs. COMPOSITION

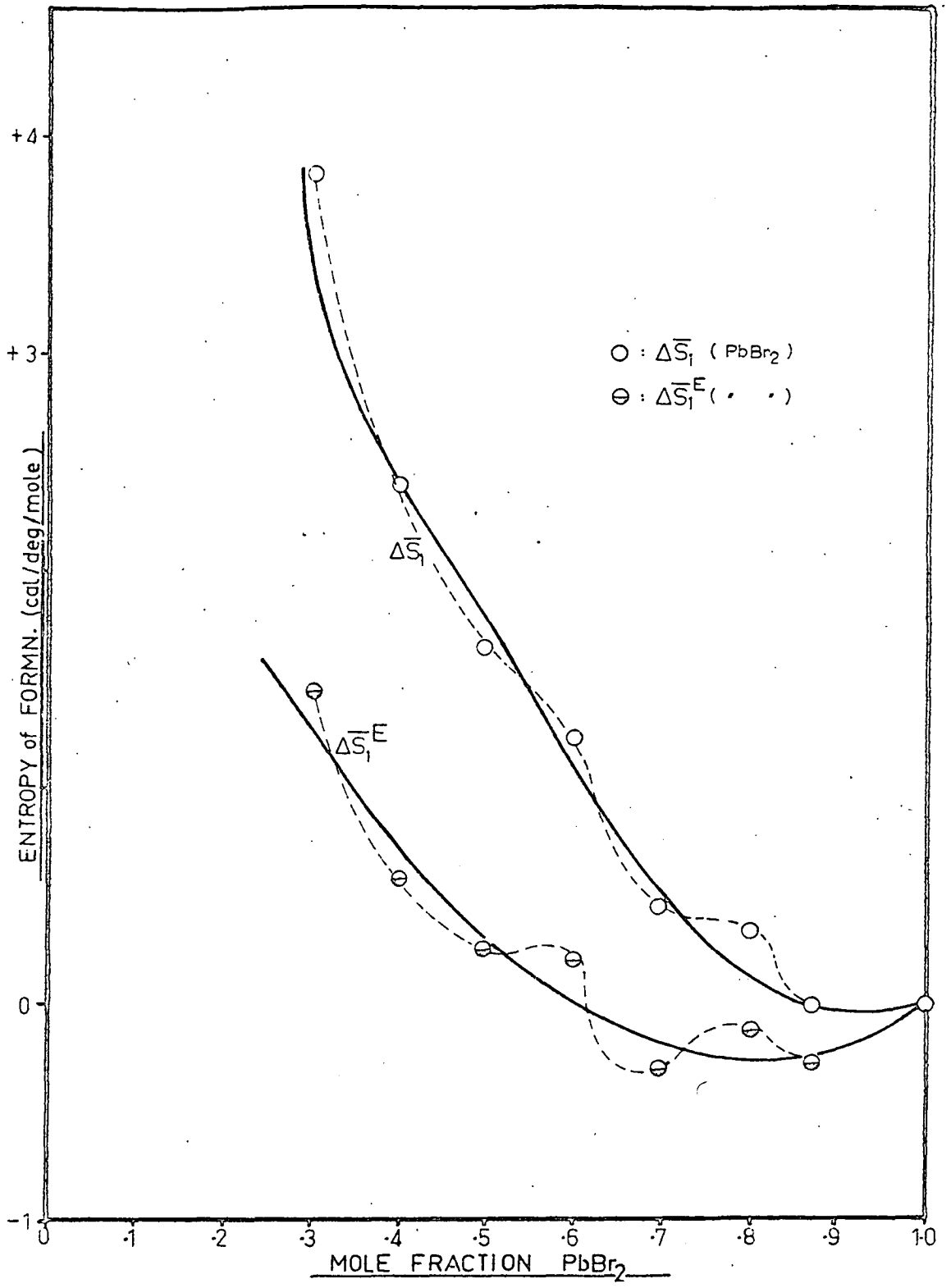



FIG. 3·13 SYSTEM $PbBr_2$–RbBr

PARTIAL & EXCESS ENTROPY $PbBr_2$ vs. COMPOSITION

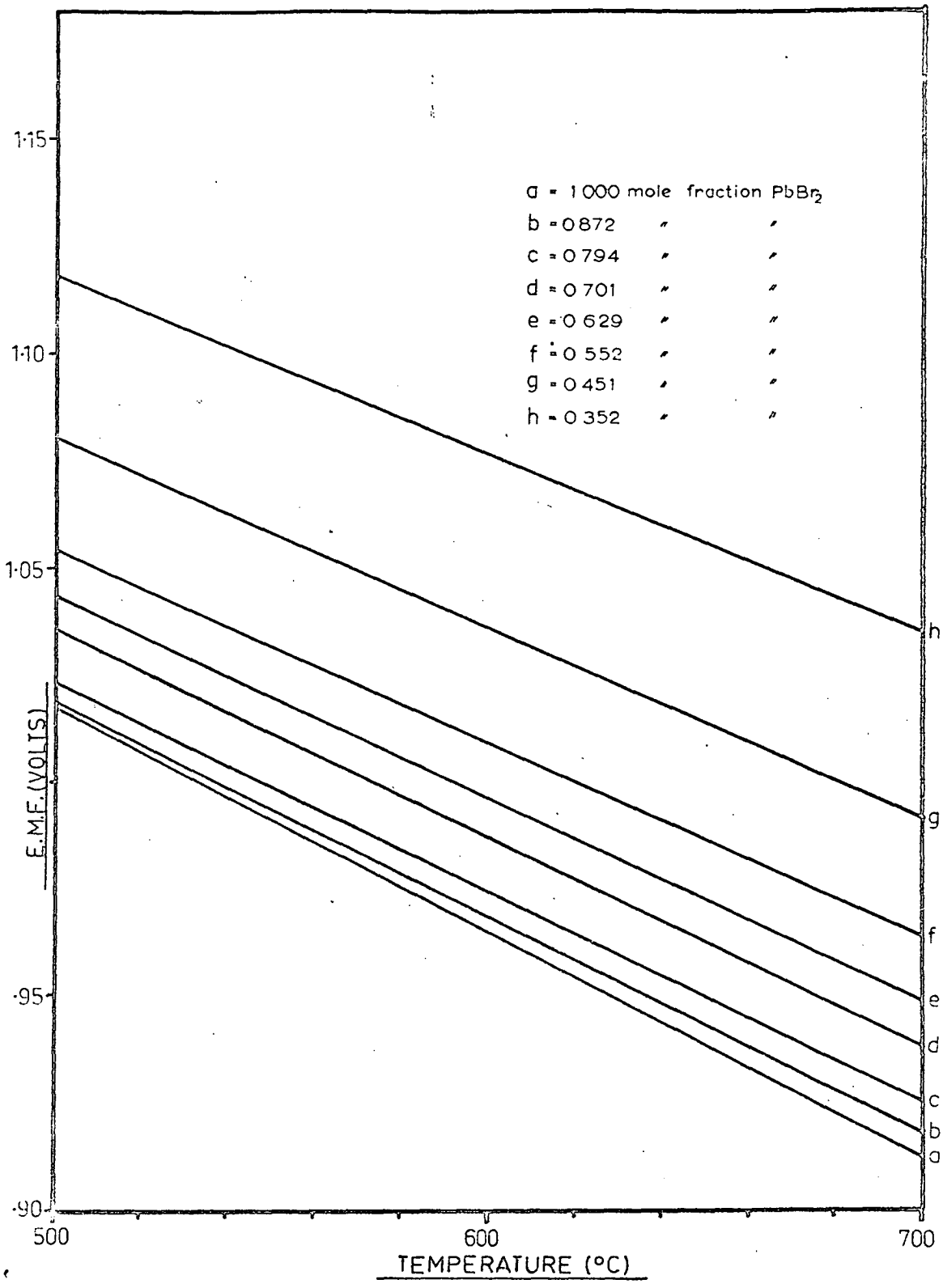



FIG. 3·14

SYSTEM $PbBr_2 - CsBr$

E.M.F. vs. TEMPERATURE

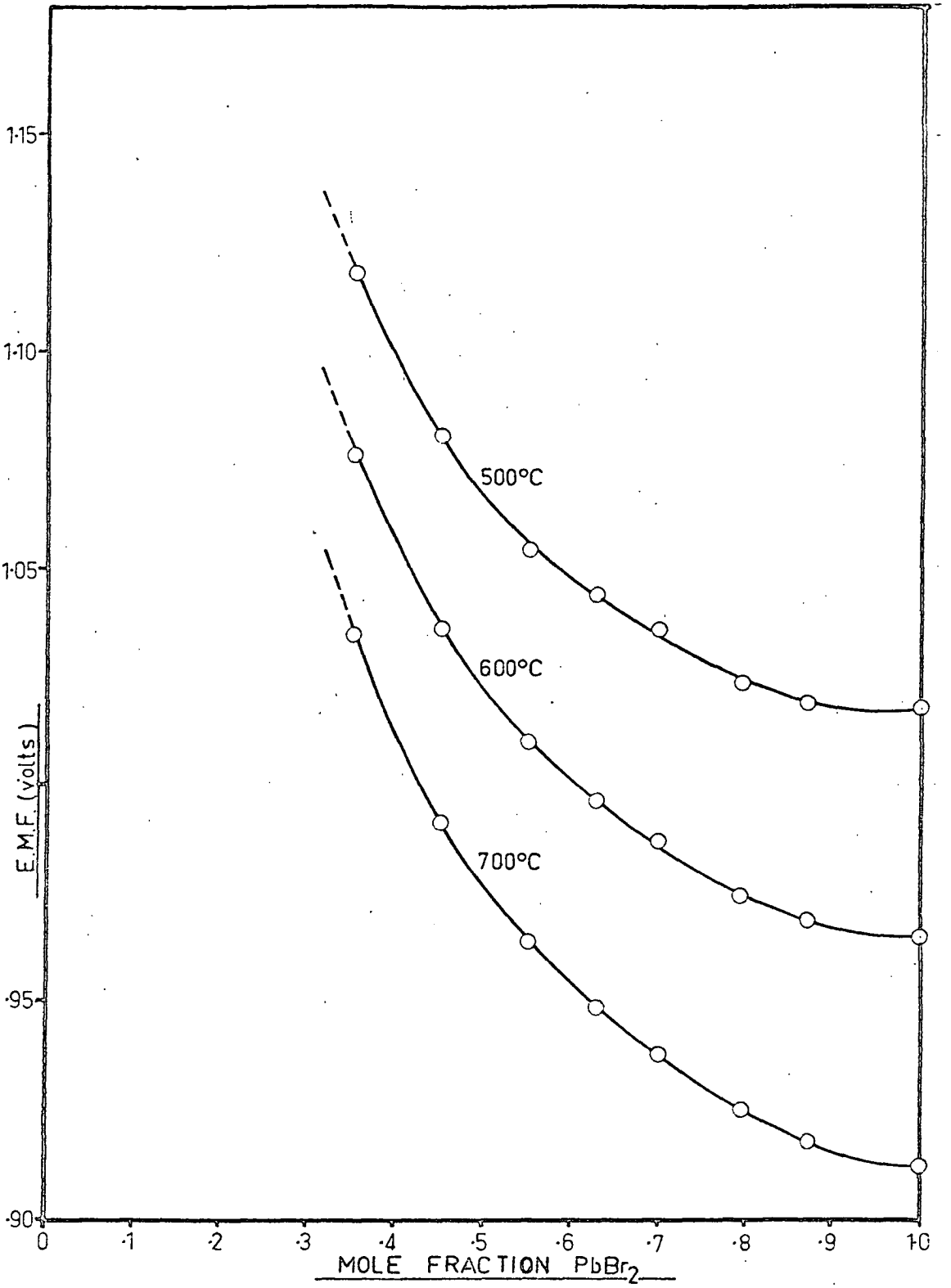



FIG. 3·15 SYSTEM $PbBr_2$–CsBr
E.M.F. vs. COMPOSITION

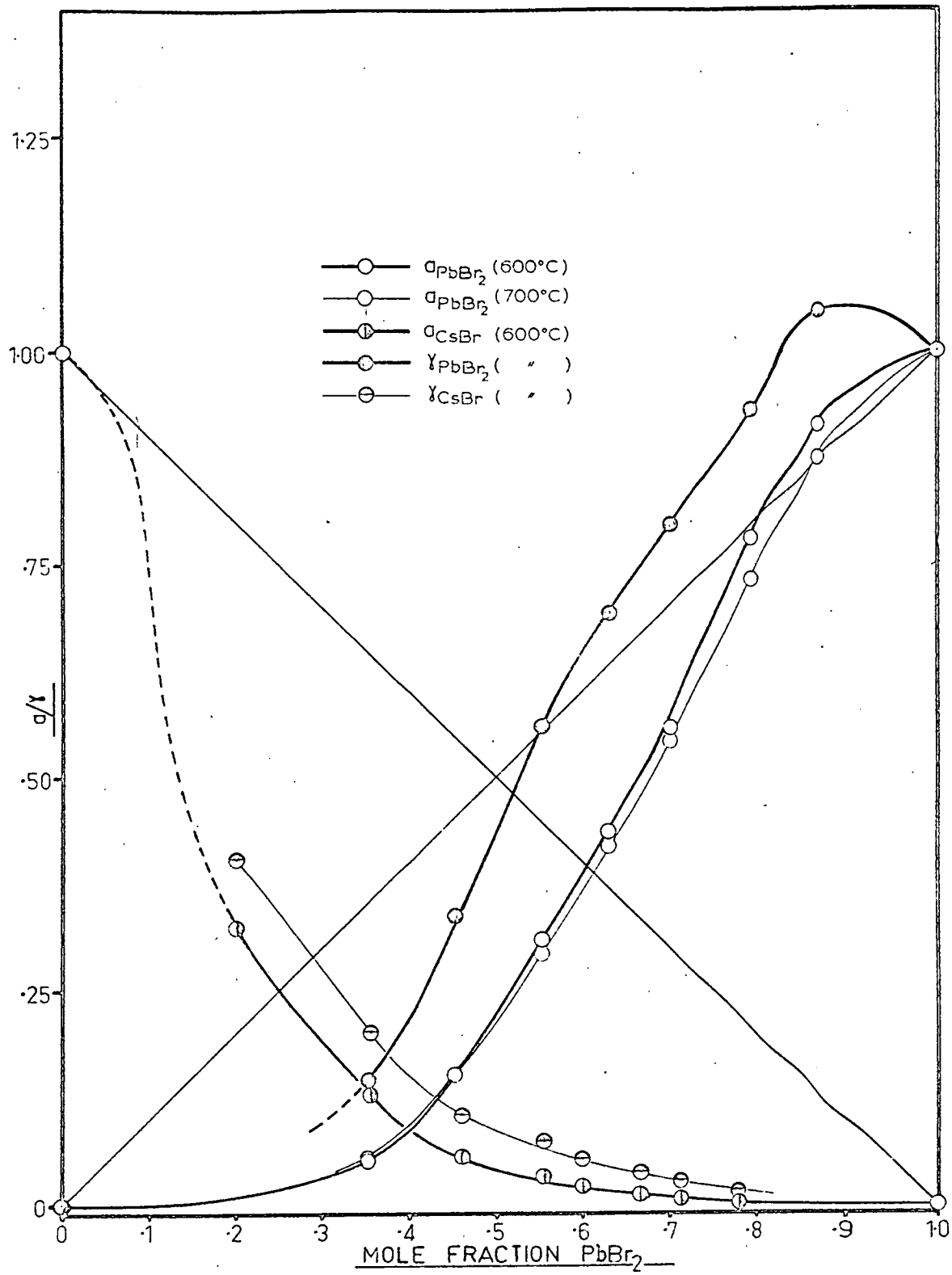



FIG. 3·16 SYSTEM $PbBr_2$ – CsBr

ACTIVITIES & ACTIVITY COEFFS vs COMPOSITION

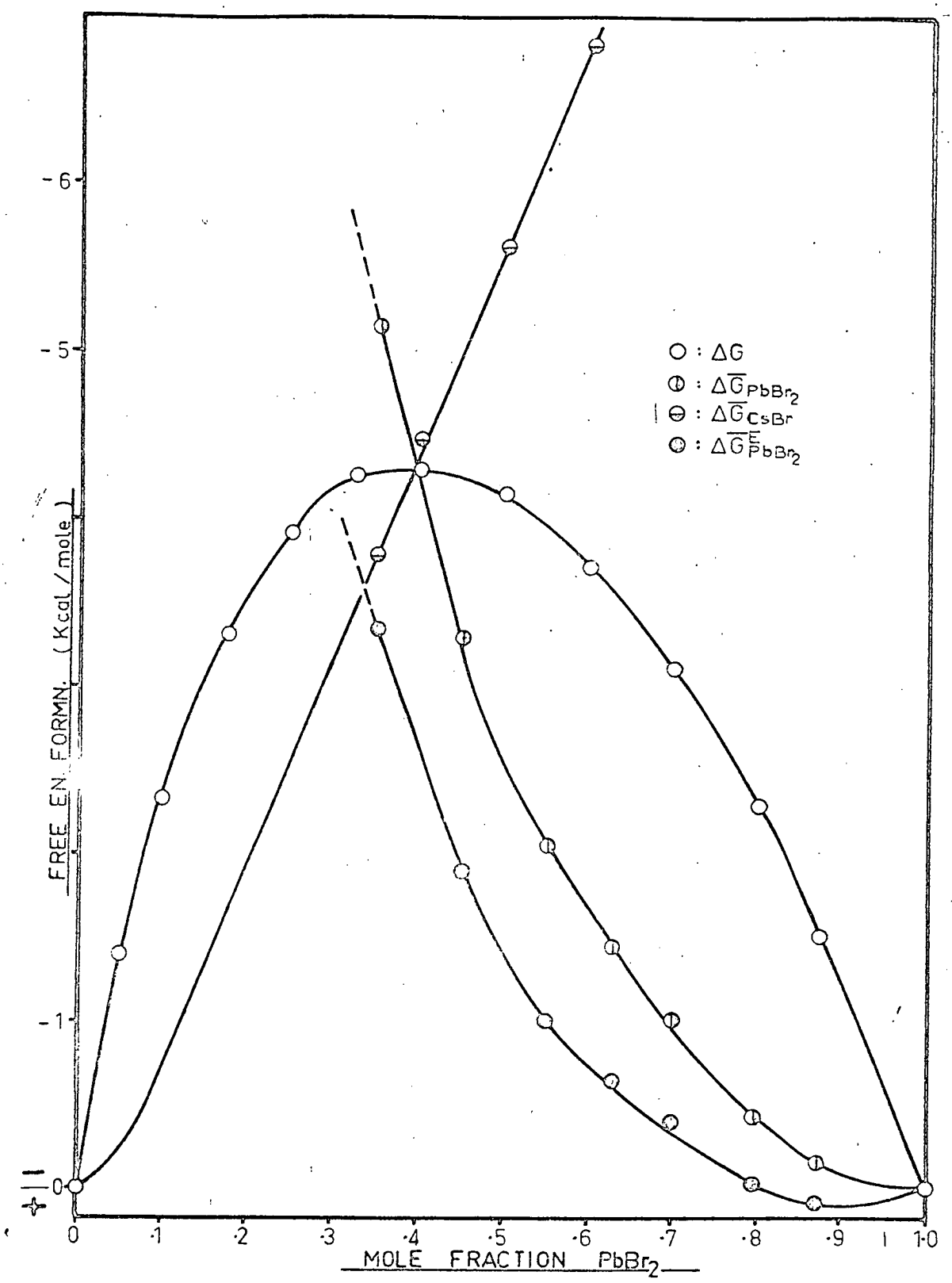



FIG. 3·17 SYSTEM $PbBr_2$–CsBr (600°)
PART., INTEG.& EXCESS ENERGIES vs COMPOSITION

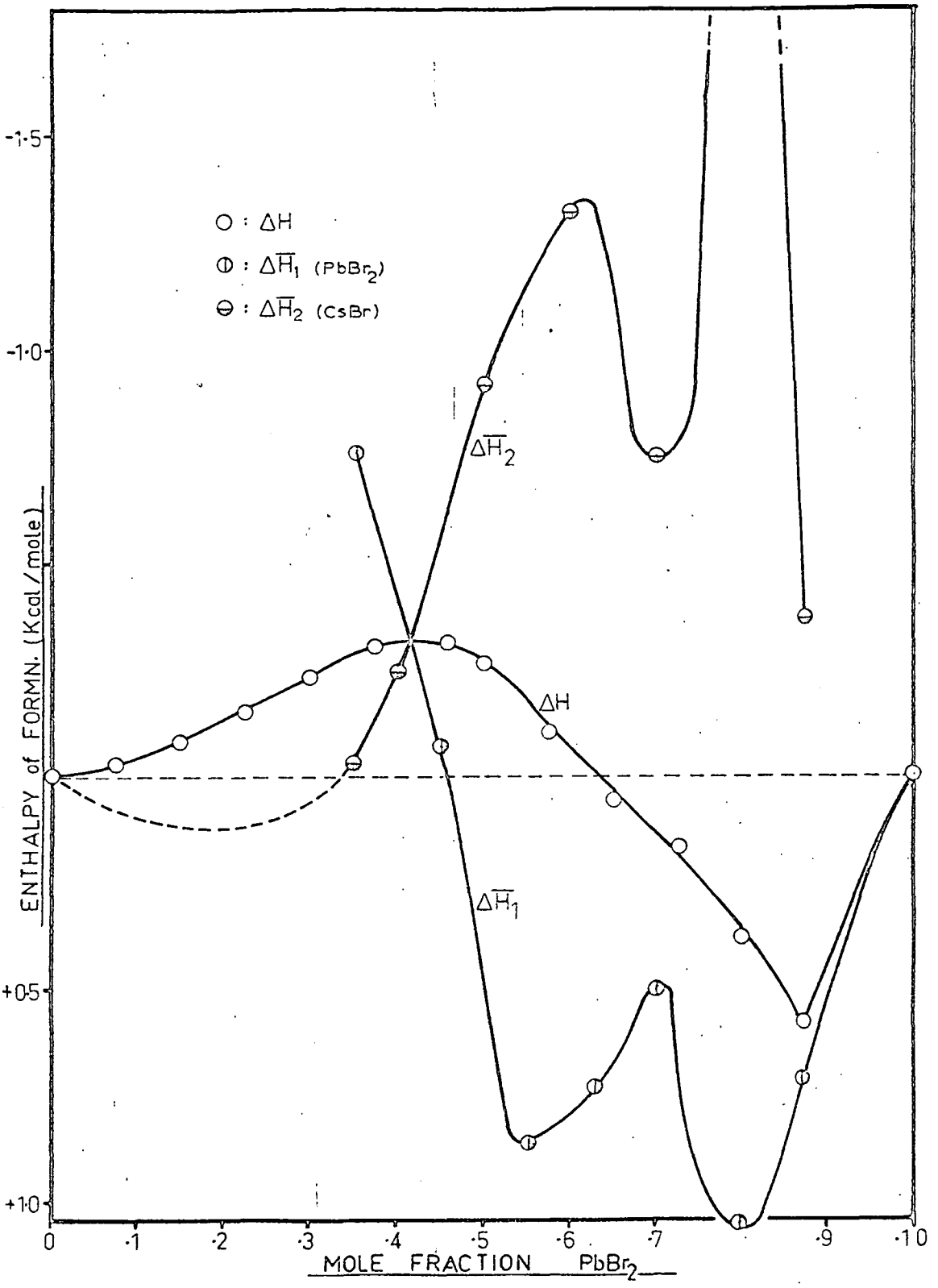



FIG. 3·18 SYSTEM $PbBr_2$–CsBr
PARTIAL & INTEGRAL ENTHALPIES vs COMPOSITION

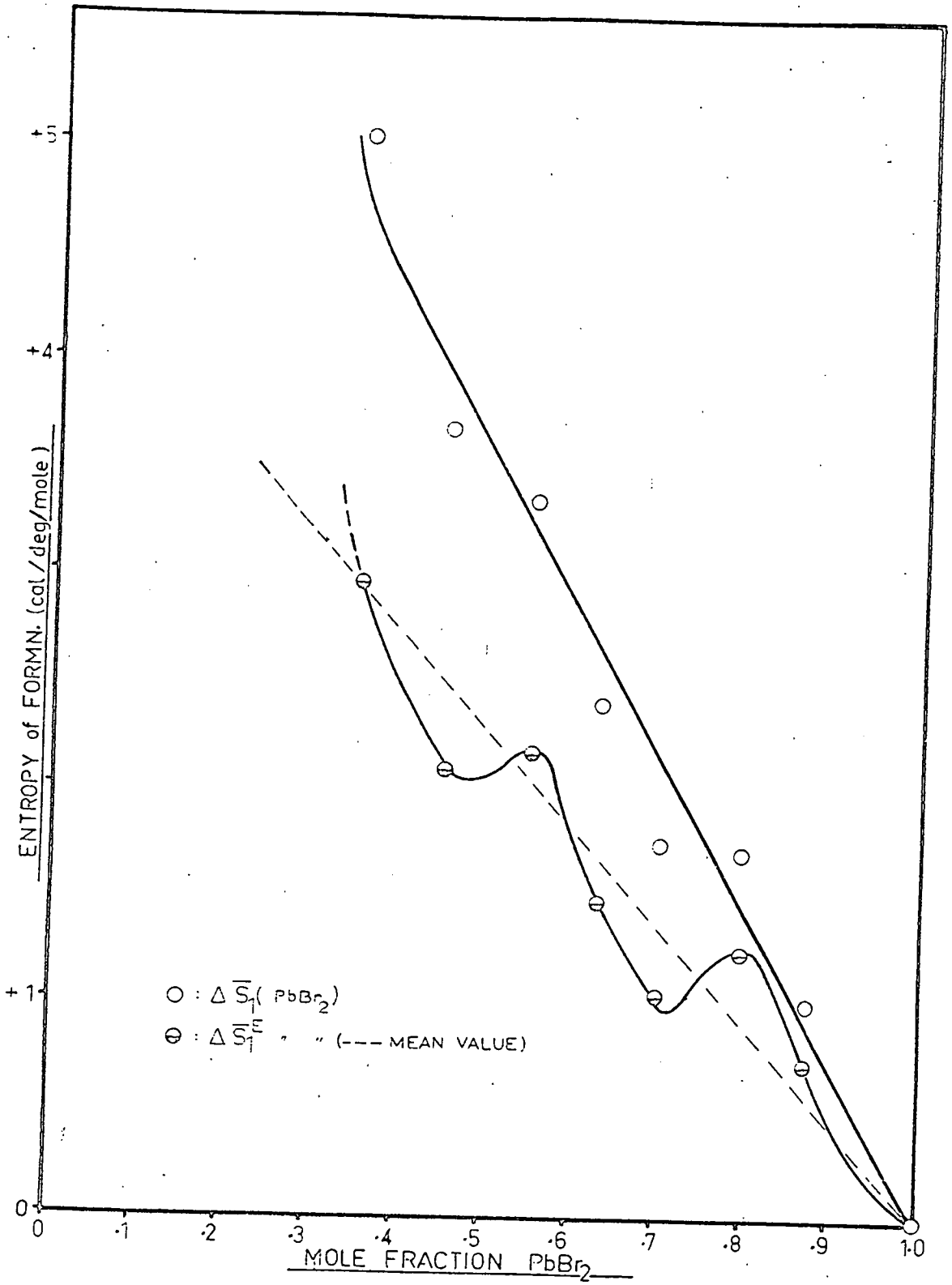



FIG. 3·19

SYSTEM $PbBr_2$–CsBr

PARTIAL & EXCESS ENTROPY $PbBr_2$ vs. COMPOSITION

## 3.2 THE THREE COMPONENT SYSTEMS $PbCl_2$-CsCl-MCl (M = Li, Na, K, Rb)

### a) Pure $PbCl_2$

The e.m.f. of the formation cell with pure $PbCl_2$ as electrolyte, was measured over the temperature range 550-900°C. The results are presented in Tables 3.21a and 3.21b and are plotted in fig. 3.20. Within the range 500-760°C there is a linear dependence of the e.m.f. on temperature, while above 760°C, the plot becomes curved and exhibits greater deviations from the extrapolated straight line plot with increasing temperature. This, by analogy to the case of zinc chloride[1], is explained by the high partial pressure of salt vapour, causing the chlorine above the melt to be depressed; this gives rise to a decrease in the e.m.f. according to the equation:

$$E_1 - E_2 = RT/zF \ln P_1/P_2 \qquad (3.1)$$

Using the data of Barton and Bloom[2], for the vapour pressure of $PbCl_2$, the partial pressure of chlorine was evaluated at each temperature ($p_{PbCl_2} + p_{Cl_2}$ = 760 mm. Hg pressure) and the e.m.f. recalculated for $p_{Cl_2}$ = 1 atmosphere, using equation 3.1. Whereas the uncorrected experimental results all showed negative deviations from the extrapolated "least squares" line, the corrected values showed much smaller positive deviations (see Table 3.21b). This could be due to non-equilibrium vapour-liquid conditions, causing a lower partial pressure of PbCl2 than for the equilibrium measurements of Barton and Bloom.

---

1. Delimarskii and Markov: "Electrochem. of Fused Salts", Sigma Press (1961)
2. Barton and Bloom: J. Phys. Chem., 60 1413 (1956)

The results of other workers are also shown graphically in fig. 3.20. The present work agrees reasonably (to within ± 7.0 mv.) with those of Lorenz and Velde[1] and Richards[2], although the temperature coefficient of the e.m.f. is closer to the latter. Other workers, such as Czepinski[3] and Grube and Rau[4], published results which were much lower than obtained in the present investigation. The early work of Czepinski[3] gave values for the e.m.f. up to 55 millivolts lower, with uncertainties of 15 millivolts, whereas the data of Grube and Rau, although 20 millivolts lower than the present work, gave reasonable agreement with respect to the temperature coefficient. The results of Hildebrand and Ruhle[5] show much greater temperature dependence than those of any other worker and this is attributed to the technique used to produce the halogen electrode[2]. In this case, the cell containing pure $PbCl_2$ was initially electrolysed to form chlorine (gas) and lead (liquid), after which the current was stopped and the potential measured. All other workers used electrodes produced in a similar manner to the ones used in the present investigation. Other work shown in fig. 3.20 is that by Lantratov and Alabyshev[6] and Wachter and Hildebrand[7].

Thermodynamic properties for pure $PbCl_2$ are listed in Table 3.22.

---


1. Lorenz and Velde: Z. anorg. u allgem. Chem., 183 81 (1929)
2. Richards: Ph.D. thesis, University of New Zealand (1956)
3. Czepinski: Z. anorg. u allgem. Chem., 19 208 (1899)
4. Grube and Rau: Z. Elektrochem., 40 352 (1934)
5. Hildebrand and Ruhle: J. Am. Chem. Soc., 49 722 (1927)
6. Lantratov and Alabyshev: Zhur. Priklad. Khim., 26 263, 353 (1953)
7. Wachter and Hildebrand: J. Am. Chem. Soc., 52 4655 (1930)

b) The binary system $PbCl_2$-CsCl

The value of e.m.f. and temperature for the formation cells containing $PbCl_2$ and CsCl as electrolyte, are found in Table 3.23, together with the deviations from the line of best fit at each temperature. The equations to these lines are listed in Table 3.24 and are plotted in fig. 3.21. In the e.m.f. isotherms (fig. 3.22), the small maximum in the vicinity of 0.85 mole fraction $PbCl_2$ may not have any significance, as the uncertainty of this point is of the order of 2.2 millivolts. It is therefore necessary to exercise care when interpreting properties in the vicinity of this composition.

The activity and activity coefficient for lead chloride are summarized in Table 3.25 and are illustrated in fig. 3.23. The dotted curves represent the smoothed values of both the activity and activity coefficient of $PbCl_2$ at 700°C. The activity and activity coefficient of CsCl, calculated by graphical integration of the Gibbs-Duhem equation, are shown in Table 3.26 and in fig. 3.23. As in the binary lead bromide systems, the uncertainty of extrapolating to infinity in the evaluation of these quantities, leads to an error of approximately $\pm$ 0.1 units for the activity of CsCl in the composition range 0.2-0.3 mole fraction $PbCl_2$. This reduces to about $\pm$ 0.02 units for compositions richer than 0.6 mole fraction $PbCl_2$.

Partial molar thermodynamic quantities and excess functions for $PbCl_2$, are listed in Table 3.27 and illustrated in figs. 3.24 and 3.25. Partial free energies of CsCl and integral free energies in the system $PbCl_2$-CsCl, calculated from equations 1.82 and 1.81 respectively, are shown in Table 3.28 and in fig. 3.24.

Assuming the uncertainty in the e.m.f. of the formation cells to be within $\pm$ 0.6 millivolts, except for the compositions 0.848, 0.485 and 0.398 mole fraction $PbCl_2$, the errors in the thermodynamic functions will be of the following order:

| | | | |
|---|---|---|---|
| $\Delta G_1$ | $\pm$ 30 cals/mole, | $\Delta \bar{G}_1$, $\Delta \bar{G}_1^E$ | $\pm$ 45 cals/mole, |
| $\Delta S_1$ | $\pm$ 0.5 cals/deg/mole, | $\Delta \bar{S}_1$, $\Delta \bar{S}_1^E$ | $\pm$ 0.8 cals/deg/mole, |
| $\Delta H_1$ | $\pm$ 350 cals/mole, | $\Delta \bar{H}_1$ | $\pm$ 500 cals/mole. |

For such compositions as 0.848 mole fraction $PbCl_2$, the uncertainty is much greater (see Table 3.24) and the validity of maxima in these regions is questionable. For the integral free energies and the derived partial quantities for the second component, it is difficult to estimate the error because of the graphical integration procedure, but the uncertainty is probably within the range $\pm$ 100-350 cals/mole for both $\Delta G$ and $\Delta \bar{G}_2$.

c) <u>The three component systems (x $PbCl_2$ + x CsCl) —— (1-2x) MCl</u>

The values for e.m.f. and temperature for the cells:

$Pb/(x\ PbCl_2 + x\ CsCl)$ —— $(1-2x)MCl/C, Cl_2$,

are found in Tables 3.29-3.32 and in figs. 3.26-3.29. E.m.f. isotherms as a function of composition are illustrated in figs. 3.30-3.33. The dashed lines in the latter represent the corresponding isotherms for the system $PbCl_2$-CsCl.

The activity and activity coefficients of $PbCl_2$ in the three component systems are summarized in Tables 3.37-3.40. Activity and activity coefficient isotherms, together with the isotherms for the system $PbCl_2$ - CsCl are plotted in figs. 3.34A-3.37A and fig. 3.38 respectively. Since the 0.50 mole fraction $PbCl_2$ + 0.50 mole fraction

CsCl mixture was not investigated, the value shown has been obtained by interpolation. The limited data available from e.m.f. measurements on the three component systems, prevented the evaluation of the activities etc. for either CsCl or MCl. The errors in activites and activity coefficients of $PbCl_2$, do not exceed $\pm$ 0.02 units for any of the systems.

The partial molar thermodynamic functions of $PbCl_2$ for each of the four systems, were calculated at three temperatures and are listed in Tables 3.41-3.44. The partial and excess molar free energies are plotted as functions of the mole fraction of lead chloride in figs. 3.39A-3.42A. In Table 3.45, the deviations of the partial molar free energies of $PbCl_2$, ( $\Delta\bar{G}_1^*$), in each of the systems (x $PbCl_2$ + x CsCl) —— (1-2x)MCl, from the binary $PbCl_2$-CsCl system at corresponding compositions of $PbCl_2$, are presented as functions of the ratio $\left[MCl\right] / \left[CsCl\right]$ . These quantities are plotted in fig. 3.43. Because the partial molar free energies of lead chloride in the two systems (x $PbCl_2$ + x CsCl) —— (1-2x)MCl and $PbCl_2$ - CsCl were obtained by interpolation at corresponding integral compositions of $PbCl_2$, it was necessary, for the plot of $\Delta\bar{G}_1^*$ as a function of the ratio (mole fraction MCl)/(mole fraction CsCl), to assume equimolar proportions of CsCl and $PbCl_2$. With reference to Tables 3.33-3.36, this can be seen to be approximately true only. This assumption led to errors in the value of $\left[MCl\right] / \left[CsCl\right]$ of approximately 10%. Errors in interpolating values of $\Delta\bar{G}_1$ from the graphs of $\Delta\bar{G}_1$ vs. composition, in the binary and three component systems, gave rise to errors in

$\Delta\bar{G}_1$* of approximately $\pm$ 200 cals/mole.

Errors in the partial thermodynamic functions were of the same order of magnitude in each of the four systems and were estimated as follows:

| | | | |
|---|---|---|---|
| $\Delta G_1$ | $\pm$ 15 cals/mole, | $\Delta\bar{G}_1$, $\Delta\bar{G}_1^E$ | $\pm$ 20 cals/mole, |
| $\Delta S_1$ | $\pm$ 0.3 cals/deg/mole, | $\Delta\bar{S}_1$, $\Delta\bar{S}_1^E$ | $\pm$ 0.5 cals/deg/mole, |
| $\Delta H_1$ | $\pm$ 180 cals/mole, | $\Delta\bar{H}_1$ | $\pm$ 300 cals/mole. |

d) <u>The three component systems (2x $PbCl_2$ + x CsCl) —— (1-3x)MCl</u>

The experimental values for e.m.f. and temperature for the formation cells:

Pb/(2x $PbCl_2$ + x CsCl) —— (1-3x)MCl/C, $Cl_2$,

are presented in Tables 3.46-3.49. The equations to the lines of best fit are summarized in Tables 3.50-3.53 and are plotted in figs. 3.44-3.47. Isotherms of e.m.f. vs. composition are also plotted in figs. 3.48-3.51.

Calculated activities and activity coefficients are found in Tables 3.54-3.57. The errors in both these quantities are similar in the four systems and are of the same order of magnitude as in the series (x $PbCl_2$ + x CsCl) —— (1-2x)MCl. Insufficient information prevented the calculation of similar quantities for either MCl or CsCl. The activities and activity coefficients for $PbCl_2$ in each system are represented in figs. 3.34B-3.37B and 3.52 respectively.

Partial molar quantities for $PbCl_2$ are found in Tables 3.58-3.61. Partial and excess free energies of $PbCl_2$ are illustrated in figs. 3.39B-3.42B, together with the values for $PbCl_2$ in the system $PbCl_2$-CsCl. As before, the value of $a_{PbCl_2}$, $\Delta\bar{G}_{PbCl_2}$, etc., for the

mixture 0.667 mole fraction $PbCl_2$ + 0.333 mole fraction CsCl, was obtained by interpolation from a plot of the corresponding thermodynamic quantity as a function of composition, for the system $PbCl_2$ - CsCl. Deviations of the partial molar free energies of $PbCl_2$ in the system (2x $PbCl_2$ + x CsCl) —— (1-3x)MCl, from those in the binary system, are given as functions of the alkali halide ratios and are set out in Table 3.62 and plotted in fig. 3.53.

The same limits of accuracy apply to both the thermodynamic quantities $\Delta\bar{G}_1$, $\Delta\bar{S}_1$, $\Delta\bar{H}_1$, etc., and to the ratio $N_{MCl}/N_{CsCl}$, in the two series (x $PbCl_2$ + x CsCl)—— (1-2x)MCl and (2x $PbCl_2$ + x CsCl) —— (1-3x)MCl.

TABLE 3.21(a)

Values of e.m.f. and temperature for the formation cell:

Pb/pure $PbCl_2$/C, $Cl_2$

| temperature (°C) | e.m.f. (volts) | $\Delta$E (mv.) | temperature (°C) | e.m.f. (volts) | $\Delta$E (mv.) |
|---|---|---|---|---|---|
| 551.6 | 1.2369 | -0.1 | 676.8 | 1.1658 | +0.4 |
| 590.0 | 1.2154 | +0.4 | 698.8 | 1.1530 | +0.2 |
| 607.0 | 1.2055 | +0.2 | 728.6 | 1.1361 | +0.4 |
| 637.6 | 1.1875 | -0.3 | 763.2 | 1.1149 | -1.0 |

Equation to line: $E = 1.5527 - (5.723 \times 10^{-4})t$

Mean deviation: = 0.4 mv.

TABLE 3.21(b)

Measured values of e.m.f. at various temperatures for the cell Pb/pure $PbCl_2$/C, $Cl_2$ and values calculated for the reduced partial pressure of chlorine due to $PbCl_2$ vapour above the melt

| temp. (°C) | e.m.f. meas. (volts) | $P_{PbCl_2}$ (mm.) | $P_{Cl_2}$ (mm.) | $E_{P_{Cl_2}}$ correction | corrected e.m.f. (volts) | △E (mv.) | |
|---|---|---|---|---|---|---|---|
| | | | | | | uncorrected | corrected |
| 800.4 | 1.0913 | 126.2 | 633.8 | 0.0084 | 1.0997 | - 3.3 | +5.1 |
| 819.0 | 1.0778 | 162.6 | 597.4 | 0.0113 | 1.0891 | - 6.2 | +5.1 |
| 853.8 | 1.0511 | 256.4 | 503.6 | 0.0200 | 1.0711 | -13.0 | +7.0 |
| 858.4 | 1.0472 | 271.0 | 489.0 | 0.0215 | 1.0687 | -14.2 | +7.3 |
| 900.1 | 1.0012 | 444.6 | 315.4 | 0.0445 | 1.0457 | -36.4 | +8.1 |

TABLE 3.22

Thermodynamic properties of pure $PbCl_2$

| temperature (°C) | △G° (K cal/mole) | △S° (cal/deg/mole) | △H° (K cal/mole) |
|---|---|---|---|
| 600 | -55.78 | | |
| 700 | -53.14 | -26.40 | -78.82 |
| 800 | -50.50 | | |

TABLE 3.23

Values of e.m.f. and temperature for the formation cells:

$Pb/PbCl_2(N_1) + CsCl(N_2)/C, Cl_2$

| composition (m.f.$PbCl_2$) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) |
|---|---|---|---|---|---|---|
| 0.886 | 539.0 | 1.2499 | -1.2 | 638.5 | 1.1945 | +1.1 |
| | 568.6 | 1.2335 | -0.4 | 686.2 | 1.1658 | 0.0 |
| | 591.2 | 1.2208 | 0.0 | 735.6 | 1.1371 | -0.1 |
| | 607.2 | 1.2115 | -0.1 | 781.0 | 1.1111 | +0.2 |
| 0.848 | 546.0 | 1.2520 | +2.3 | 666.0 | 1.1866 | +2.4 |
| | 588.0 | 1.2242 | -2.6 | 695.5 | 1.1644 | -3.7 |
| | 590.1 | 1.2257 | +0.1 | 721.6 | 1.1563 | +2.3 |
| | 606.1 | 1.2195 | +0.6 | 748.4 | 1.1343 | -4.9 |
| | 621.3 | 1.2084 | -0.2 | 778.0 | 1.1276 | -4.6 |
| | 636.2 | 1.1971 | -3.4 | 800.9 | 1.1105 | 0.0 |
| 0.789 | 554.2 | 1.2443 | -1.7 | 697.0 | 1.1688 | +0.1 |
| | 581.0 | 1.2341 | +2.6 | 723.8 | 1.1550 | +0.9 |
| | 604.0 | 1.2177 | -1.4 | 744.0 | 1.1425 | -0.7 |
| | 633.4 | 1.2044 | +1.3 | 753.6 | 1.1379 | -0.1 |
| | 651.4 | 1.1932 | -0.2 | 789.4 | 1.1188 | +0.2 |
| | 672.4 | 1.1819 | -0.1 | 796.2 | 1.1150 | +0.1 |
| 0.745 | 540.0 | 1.2574 | -0.9 | 751.4 | 1.1419 | -0.6 |
| | 572.0 | 1.2423 | +1.5 | 776.6 | 1.1288 | +0.1 |
| | 601.8 | 1.2235 | -1.0 | 781.0 | 1.1260 | -0.3 |
| | 632.7 | 1.2077 | +0.2 | 802.9 | 1.1145 | -0.2 |
| | 660.5 | 1.1928 | +0.5 | 828.6 | 1.1005 | +0.2 |
| | 691.0 | 1.1754 | -0.2 | 834.9 | 1.0968 | 0.0 |
| | 721.8 | 1.1590 | +0.3 | | | |
| 0.676 | 582.0 | 1.2441 | +0.1 | 741.0 | 1.1560 | -0.6 |
| | 590.6 | 1.2391 | -0.2 | 759.0 | 1.1466 | -0.2 |
| | 621.0 | 1.2226 | 0.0 | 786.0 | 1.1319 | 0.0 |
| | 649.0 | 1.2075 | +0.3 | 795.0 | 1.1272 | +0.2 |

Table 3.23 (contd.)

| composition (m.f.$PbCl_2$) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) |
|---|---|---|---|---|---|---|
| 0.676 (contd.) | 673.2 | 1.1937 | -0.2 | 823.0 | 1.1115 | -0.1 |
| | 696.4 | 1.1818 | +0.6 | 827.0 | 1.1094 | 0.0 |
| | 722.4 | 1.1671 | +0.2 | | | |
| 0.622 | 592.7 | 1.2496 | -1.3 | 693.6 | 1.1945 | 0.0 |
| | 609.3 | 1.2410 | -0.7 | 716.3 | 1.1844 | +2.5 |
| | 620.0 | 1.2359 | +0.2 | 752.4 | 1.1635 | +1.8 |
| | 630.9 | 1.2281 | -1.5 | 778.3 | 1.1472 | 0.0 |
| | 652.2 | 1.2169 | -0.8 | 801.1 | 1.1344 | -0.1 |
| | 663.6 | 1.2117 | +0.4 | | | |
| 0.485 | 613.0 | 1.2673 | +0.3 | 749.9 | 1.1995 | +2.4 |
| | 630.9 | 1.2584 | +0.4 | 775.1 | 1.1826 | -1.6 |
| | 663.3 | 1.2417 | +0.4 | 787.2 | 1.1806 | +2.6 |
| | 686.6 | 1.2281 | -1.3 | 820.5 | 1.1608 | -0.2 |
| | 710.2 | 1.2192 | +1.8 | 824.8 | 1.1590 | +0.2 |
| | 722.0 | 1.2094 | -1.9 | 849.9 | 1.1460 | 0.0 |
| | 744.6 | 1.1974 | -2.4 | | | |
| 0.398 | 615.0 | 1.3036 | +3.5 | 750.8 | 1.2314 | +0.8 |
| | 640.6 | 1.2846 | -2.4 | 767.0 | 1.2200 | -2.3 |
| | 663.3 | 1.2753 | -0.1 | 787.0 | 1.2132 | +1.1 |
| | 679.3 | 1.2672 | 0.0 | 798.6 | 1.2053 | -0.9 |
| | 690.0 | 1.2595 | -2.2 | 821.7 | 1.1947 | +0.3 |
| | 712.0 | 1.2534 | +2.9 | 824.9 | 1.1942 | +1.5 |
| | 730.8 | 1.2386 | -2.3 | 851.3 | 1.1791 | -0.1 |
| 0.307 | 602.2 | 1.3446 | +1.1 | 742.6 | 1.2741 | 0.0 |
| | 627.0 | 1.3312 | -0.1 | 756.7 | 1.2660 | -1.1 |
| | 659.0 | 1.3160 | +1.4 | 783.0 | 1.2549 | +0.8 |
| | 685.2 | 1.3017 | -0.8 | 788.2 | 1.2512 | -0.3 |
| | 704.0 | 1.2934 | +0.2 | 819.6 | 1.2316 | +1.6 |
| | 725.0 | 1.2815 | -1.3 | 822.6 | 1.2345 | 0.0 |

TABLE 3.24

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:

$Pb/PbCl_2(N_1) + CsCl(N_2)/C, Cl_2$

| composition (m.f. $PbCl_2$) | e.m.f. at temperature t°C (volts) | mean deviation of exptl. pts. from line (mv.) |
|---|---|---|
| 0.886 | $1.5632 - (5.791 \times 10^{-4})t$ | 0.4 |
| 0.848 | $1.5479 - (5.461 \times 10^{-4})t$ | 2.2 |
| 0.789 | $1.5463 - (5.418 \times 10^{-4})t$ | 0.8 |
| 0.745 | $1.5540 - (5.476 \times 10^{-4})t$ | 0.5 |
| 0.676 | $1.5639 - (5.496 \times 10^{-4})t$ | 0.2 |
| 0.622 | $1.5822 - (5.589 \times 10^{-4})t$ | 0.8 |
| 0.485 | $1.5802 - (5.109 \times 10^{-4})t$ | 1.1 |
| 0.398 | $1.6145 - (5.113 \times 10^{-4})t$ | 1.5 |
| 0.307 | $1.6415 - (4.948 \times 10^{-4})t$ | 0.7 |

TABLE 3.25

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in the system $PbCl_2$-CsCl

| composition (m.f.$PbCl_2$) | Activity $PbCl_2$ | | | Error $a_{PbCl_2}$ (700°C) | Activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | | 600°C | 700°C | 800°C |
| 0.886 | 0.8435 | 0.8730 | 0.8976 | $\pm$0.011 | 0.9520 | 0.9853 | 1.0131 |
| 0.848 | 0.7485 | 0.7247 | 0.7060 | $\pm$0.038 | 0.8827 | 0.8546 | 0.8325 |
| 0.789 | 0.7290 | 0.7009 | 0.6776 | $<\pm$0.005 | 0.9240 | 0.8883 | 0.8588 |
| 0.745 | 0.6519 | 0.6418 | 0.6351 | " | 0.8750 | 0.8615 | 0.8525 |
| 0.676 | 0.5174 | 0.5241 | 0.5308 | " | 0.7654 | 0.7753 | 0.7852 |
| 0.622 | 0.3682 | 0.3956 | 0.4193 | " | 0.5920 | 0.6360 | 0.6741 |
| 0.485 | 0.1806 | 0.1862 | 0.1909 | " | 0.3724 | 0.3839 | 0.3936 |
| 0.398 | 0.0732 | 0.0779 | 0.0787 | " | 0.1839 | 0.1957 | 0.1977 |
| 0.307 | 0.0275 | 0.0331 | 0.0384 | " | 0.0896 | 0.1078 | 0.1251 |
| 1.000 | 1.0000 | 1.0000 | 1.0000 | " | 1.0000 | 1.0000 | 1.0000 |

TABLE 3.26

Value of the activity and activity coefficient of CsCl (700°C) at different compositions in the system $PbCl_2$-CsCl

| composition (m.f. CsCl) | activity CsCl (700°C) | activity coefficient (700°C) |
|---|---|---|
| 0.118 | 0.0033 | 0.0281 |
| 0.133 | 0.0040 | 0.0302 |
| 0.154 | 0.0053 | 0.0347 |
| 0.182 | 0.0074 | 0.0406 |
| 0.222 | 0.0103 | 0.0462 |
| 0.267 | 0.0138 | 0.0515 |
| 0.333 | 0.0201 | 0.0605 |
| 0.400 | 0.0300 | 0.0749 |
| 0.500 | 0.0542 | 0.1083 |
| 0.571 | 0.0807 | 0.1414 |
| 0.667 | 0.1471 | 0.2205 |
| 0.769 | 0.2702 | 0.3514 |
| 0.870 | 0.4793 | 0.5509 |

## TABLE 3.27

**Partial molar thermodynamic functions of $PbCl_2$ in the system $PbCl_2$-CsCl**

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 700°C | | | | | |
| mole fraction $PbCl_2$ | | 1.000 | 0.886 | 0.848 | 0.789 | 0.745 | 0.676 | 0.622 | 0.485 | 0.398 | 0.307 |
| $\Delta G_1$ | (K cal/mole) | -53.14 | -53.40 | -53.76 | -53.82 | -54.00 | -54.39 | -54.93 | -56.39 | -57.96 | -59.74 |
| $\Delta G_1$ | (cal/deg/mole) | -26.40 | -26.71 | -25.19 | -24.99 | -25.26 | -25.35 | -25.78 | -23.57 | -23.58 | -22.82 |
| $\Delta H_1$ | (K cal/mole) | -78.82 | -79.39 | -78.27 | -78.14 | -78.57 | -79.06 | -80.02 | -79.31 | -80.91 | -81.94 |
| $\Delta \bar{G}_1$ | (K cal/mole) | | - 0.26 | - 0.62 | - 0.69 | - 0.86 | - 1.25 | - 1.80 | - 3.25 | - 4.82 | - 6.60 |
| $\Delta \bar{S}_1$ | (cal/deg/mole) | | - 0.31 | + 1.21 | + 1.41 | + 1.39 | + 1.05 | + 0.62 | + 2.83 | + 2.81 | + 3.58 |
| $\Delta \bar{H}_1$ | (K cal/mole) | | - 0.57 | + 0.55 | + 0.68 | + 0.25 | - 0.24 | - 1.20 | - 0.50 | - 2.09 | - 3.12 |
| $\Delta \bar{G}_1^E$ | (K cal/mole) | | - 0.03 | - 0.30 | - 0.23 | - 0.29 | - 0.49 | - 0.87 | - 1.85 | - 3.15 | - 4.31 |
| $\Delta \bar{S}_1^E$ | (cal/deg/mole) | | - 0.55 | + 0.88 | + 0.94 | + 0.55 | + 0.27 | - 0.33 | + 1.39 | + 0.98 | + 1.23 |
| | | | | | 600°C | | | | | |
| $\Delta G_1$ | (K cal/mole) | -55.78 | -56.07 | -56.28 | -56.33 | -56.52 | -56.92 | -57.51 | -58.75 | -60.32 | -62.02 |
| $\Delta \bar{G}_1$ | (K cal/mole) | | - 0.30 | - 0.50 | - 0.55 | - 0.74 | - 1.14 | - 1.73 | - 2.97 | - 4.54 | - 6.24 |
| $\Delta \bar{G}_1^E$ | (K cal/mole) | | - 0.09 | - 0.22 | - 0.14 | - 0.23 | - 0.46 | - 0.91 | - 1.71 | - 2.94 | - 4.19 |
| | | | | | 800°C | | | | | |
| $\Delta G_1$ | (K cal/mole) | -50.50 | -50.73 | -51.24 | -51.33 | -51.47 | -51.85 | -52.36 | -54.03 | -55.60 | -57.46 |
| $\Delta \bar{G}_1$ | (K cal/mole) | | - 0.23 | - 0.74 | - 0.83 | - 0.97 | - 1.35 | - 1.85 | - 3.53 | - 5.10 | - 6.96 |
| $\Delta \bar{G}_1^E$ | (K cal/mole) | | + 0.03 | - 0.39 | - 0.32 | - 0.34 | - 0.51 | - 0.84 | - 1.99 | - 3.46 | - 4.43 |

TABLE 3.28

Integral free energy for the system $PbCl_2$-CsCl and partial molar free energy of CsCl at 700°C as a function of composition

| | | | | | |
|---|---|---|---|---|---|
| mole fraction $PbCl_2$ | 1.00 | 0.90 | 0.80 | 0.70 | 0.60 |
| $\Delta G$ (K cal/mole) | 0.00 | - 1.59 | - 2.84 | - 3.82 | -4.61 |
| $\Delta\bar{G}_2$ (K cal/mole) | | -13.20 | -11.50 | -10.23 | -8.58 |
| mole fraction $PbCl_2$ | 0.50 | 0.40 | 0.30 | 0.20 | 0.10 |
| $\Delta G$ (K cal/mole) | -5.16 | - 5.42 | - 5.37 | - 4.93 | -3.50 |
| $\Delta\bar{G}_2$ (K cal/mole) | -7.26 | - 5.80 | (-5.18 at 0.35 m.f. $PbCl_2$) | | |

TABLE 3.29

Values of e.m.f. and temperature for the formation cells:

$Pb/(x\ PbCl_2 + x\ CsCl)$ —— $(1-2x)$ LiCl/C, $Cl_2$

| composition (m.f.$PbCl_2$) | temp. (°C) | e.m.f. (volts) | $\Delta E$ (mv.) | temp. (°C) | e.m.f. (volts) | $\Delta E$ (mv.) |
|---|---|---|---|---|---|---|
| 0.399 | 649.6 | 1.2423 | +0.1 | 755.2 | 1.1818 | +0.1 |
| | 676.8 | 1.2264 | -0.2 | 782.0 | 1.1665 | +0.2 |
| | 703.6 | 1.2110 | -0.2 | 805.1 | 1.1529 | -0.2 |
| | 729.0 | 1.1971 | +0.4 | 827.3 | 1.1404 | 0.0 |
| 0.324 | 652.6 | 1.2470 | +0.5 | 753.0 | 1.1970 | +0.2 |
| | 679.8 | 1.2324 | -0.6 | 779.1 | 1.1840 | +0.1 |
| | 704.2 | 1.2207 | -0.3 | 803.5 | 1.1716 | -0.3 |
| | 728.0 | 1.2094 | +0.2 | 821.7 | 1.1631 | +0.2 |
| 0.245 | 640.6 | 1.2552 | +0.3 | 747.0 | 1.2070 | -0.4 |
| | 667.8 | 1.2427 | 0.0 | 771.2 | 1.1966 | 0.0 |
| | 693.4 | 1.2314 | +0.1 | 801.9 | 1.1830 | +0.1 |
| | 720.4 | 1.2193 | 0.0 | 837.4 | 1.1669 | -0.2 |
| 0.150 | 643.0 | 1.2599 | -0.5 | 746.4 | 1.2151 | +0.5 |
| | 670.7 | 1.2478 | -0.3 | 770.0 | 1.2041 | 0.0 |
| | 695.5 | 1.2372 | 0.0 | 801.4 | 1.1903 | +0.1 |
| | 721.0 | 1.2262 | +0.3 | 829.9 | 1.1775 | -0.1 |

TABLE 3.30

Values of e.m.f. and temperature for the formation cells:

$Pb/(x\ PbCl_2 + x\ CsCl) \text{ —— } (1-2x)\ NaCl/C,\ Cl_2$

| composition (m.f.$PbCl_2$) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) |
|---|---|---|---|---|---|---|
| 0.398 | 608.2 | 1.2777 | +0.6 | 727.7 | 1.2159 | +0.4 |
| | 634.0 | 1.2637 | -0.1 | 757.0 | 1.2004 | 0.0 |
| | 655.0 | 1.2525 | -0.5 | 782.0 | 1.1878 | +0.2 |
| | 680.6 | 1.2396 | -0.2 | 710.0 | 1.1727 | -0.4 |
| | 703.6 | 1.2285 | +0.5 | | | |
| 0.329 | 674.8 | 1.2480 | -0.2 | 767.0 | 1.2028 | 0.0 |
| | 695.5 | 1.2380 | 0.0 | 793.6 | 1.1895 | -0.1 |
| | 721.6 | 1.2256 | +0.5 | 815.3 | 1.1789 | 0.0 |
| | 744.0 | 1.2141 | 0.0 | 840.1 | 1.1668 | +0.1 |
| 0.250 | 676.8 | 1.2593 | +0.4 | 780.4 | 1.2115 | +0.3 |
| | 702.4 | 1.2472 | +0.1 | 803.5 | 1.2004 | -0.1 |
| | 726.2 | 1.2353 | -0.8 | 830.1 | 1.1882 | -0.1 |
| | 752.8 | 1.2240 | +0.1 | 851.1 | 1.1785 | -0.1 |
| 0.145 | 755.8 | 1.2382 | +0.1 | 829.9 | 1.2070 | +0.2 |
| | 781.4 | 1.2273 | 0.0 | 855.1 | 1.1958 | -0.4 |
| | 802.6 | 1.2183 | 0.0 | | | |

TABLE 3.31

Values of e.m.f. and temperature for the formation cells:

$Pb/(x\ PbCl_2 + x\ CsCl) \text{ —— } (1-2x)\ KCl/C, Cl_2$

| composition (m.f.$PbCl_2$) | temp. (°C) | e.m.f. (volts) | △E (mv.) | temp. (°C) | e.m.f. (volts) | △E (mv.) |
|---|---|---|---|---|---|---|
| 0.396 | 652.0 | 1.2646 | +0.2 | 753.0 | 1.2173 | +0.3 |
| | 674.2 | 1.2535 | -0.5 | 777.6 | 1.2052 | -0.2 |
| | 699.3 | 1.2426 | +0.4 | 802.1 | 1.1938 | -0.1 |
| | 726.5 | 1.2294 | 0.0 | 835.1 | 1.1783 | -0.1 |
| 0.322 | 652.0 | 1.2933 | 0.0 | 751.4 | 1.2464 | +0.7 |
| | 676.5 | 1.2812 | -0.3 | 776.0 | 1.2329 | -1.0 |
| | 701.7 | 1.2706 | +1.1 | 802.5 | 1.2212 | 0.0 |
| | 724.0 | 1.2582 | -0.6 | 828.1 | 1.2091 | +0.1 |
| 0.248 | 669.5 | 1.3063 | -0.3 | 768.6 | 1.2592 | +0.3 |
| | 695.5 | 1.2938 | -0.3 | 793.1 | 1.2471 | 0.0 |
| | 721.0 | 1.2821 | +0.3 | 822.2 | 1.2333 | +0.2 |
| | 744.0 | 1.2707 | -0.1 | 850.1 | 1.2196 | -0.1 |

TABLE 3.32

Values of e.m.f. and temperature for the formation cells:

$Pb/(x\ PbCl_2 + x\ CsCl) \text{ —— } (1-2x)\ RbCl/C,\ Cl_2$

| composition (m.f.$PbCl_2$) | temp. (°C) | e.m.f. (volts) | $\triangle E$ (mv.) | temp. (°C) | e.m.f. (volts) | $\triangle E$ (mv.) |
|---|---|---|---|---|---|---|
| 0.396 | 644.9 | 1.2797 | +0.3 | 753.6 | 1.2277 | +0.7 |
| | 672.0 | 1.2662 | -0.1 | 780.0 | 1.2145 | +0.2 |
| | 698.0 | 1.2538 | 0.0 | 809.1 | 1.2006 | +0.3 |
| | 725.0 | 1.2402 | -0.6 | 832.0 | 1.1887 | -0.5 |
| 0.322 | 637.0 | 1.3130 | +0.5 | 741.8 | 1.2629 | -0.5 |
| | 663.6 | 1.3000 | 0.0 | 778.2 | 1.2463 | +0.2 |
| | 690.8 | 1.2876 | +0.3 | 805.7 | 1.2337 | +0.2 |
| | 717.6 | 1.2743 | -0.4 | | | |
| 0.250 | 621.6 | 1.3487 | -0.4 | 731.5 | 1.2965 | +0.5 |
| | 649.0 | 1.3356 | -0.2 | 758.2 | 1.2830 | -0.1 |
| | 675.3 | 1.3227 | -0.4 | 785.9 | 1.2696 | -0.1 |
| | 704.0 | 1.3097 | +0.4 | 810.1 | 1.2583 | +0.2 |

## TABLE 3.33

**Relationship between e.m.f. and temperatute from the lines of best fit for the formation cells:**

**$Pb/(x\ PbCl_2 + x\ CsCl)$ —— $(1-2x)$ LiCl/C, $Cl_2$**

| composition | | | e.m.f. at temp. t°C (volts) | mean deviation mV |
|---|---|---|---|---|
| m.f.$PbCl_2$ | m.f. CsCl | m.f. LiCl | | |
| 0.399 | 0.406 | 0.195 | $1.6142 - (5.727 \times 10^{-4})t$ | 0.2 |
| 0.324 | 0.330 | 0.345 | $1.5692 - (4.945 \times 10^{-4})t$ | 0.3 |
| 0.245 | 0.258 | 0.497 | $1.5407 - (4.462 \times 10^{-4})t$ | 0.15 |
| 0.150 | 0.154 | 0.696 | $1.5454 - (4.432 \times 10^{-4})t$ | 0.2 |

## TABLE 3.34

**Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:**

**$Pb/(x\ PbCl_2 + x\ CsCl)$ —— $(1-2x)$ NaCl/C, $Cl_2$**

| composition | | | e.m.f. at temp. t°C (volts) | mean deviation mV |
|---|---|---|---|---|
| m.f.$PbCl_2$ | m.f.CsCl | m.f.NaCl | | |
| 0.398 | 0.402 | 0.199 | $1.5906 - (5.154 \times 10^{-4})t$ | 0.3 |
| 0.329 | 0.325 | 0.346 | $1.5810 - (4.932 \times 10^{-4})t$ | 0.1 |
| 0.250 | 0.251 | 0.499 | $1.5704 - (4.603 \times 10^{-4})t$ | 0.2 |
| 0.145 | 0.153 | 0.702 | $1.5564 - (4.212 \times 10^{-4})t$ | 0.1 |

TABLE 3.35

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:

$Pb/(x\ PbCl_2 + x\ CsCl)$ —— $(1-2x)$ KCl/C, $Cl_2$

| composition | | | e.m.f. at temp. t°C (volts) | mean deviation mV |
|---|---|---|---|---|
| m.f.$PbCl_2$ | m.f.CsCl | m.f.KCl | | |
| 0.396 | 0.408 | 0.197 | $1.5708 - (4.699 \times 10^{-4})t$ | 0.2 |
| 0.322 | 0.333 | 0.345 | $1.6053 - (4.786 \times 10^{-4})t$ | 0.5 |
| 0.248 | 0.249 | 0.503 | $1.6290 - (4.815 \times 10^{-4})t$ | 0.2 |

TABLE 3.36

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:

$Pb/(x\ PbCl_2 + x\ CsCl)$ —— $(1-2x)$ RbCl/C, $Cl_2$

| composition | | | e.m.f. at temp. t°C (volts) | mean deviation mV |
|---|---|---|---|---|
| m.f.$PbCl_2$ | m.f.CsCl | m.f.RbCl | | |
| 0.396 | 0.410 | 0.194 | $1.5900 - (4.817 \times 10^{-4})t$ | 0.3 |
| 0.322 | 0.331 | 0.347 | $1.6107 - (4.682 \times 10^{-4})t$ | 0.3 |
| 0.250 | 0.255 | 0.495 | $1.6491 - (4.827 \times 10^{-4})t$ | 0.3 |

TABLE 3.37

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in ;the system (x $PbCl_2$ + x CsCl) —— (1-2x) LiCl

| composition (m.f.$PbCl_2$) | activity $PbCl_2$ | | | activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | 600°C | 700°C | 800°C |
| 0.399 | 0.1962 | 0.2325 | 0.2670 | 0.4921 | 0.5831 | 0.6697 |
| 0.324 | 0.1866 | 0.1846 | 0.1825 | 0.5752 | 0.5691 | 0.5626 |
| 0.245 | 0.1842 | 0.1623 | 0.1468 | 0.7509 | 0.6616 | 0.5985 |
| 0.150 | 0.1550 | 0.1380 | 0.1259 | 0.0361 | 0.9225 | 0.8416 |

TABLE 3.38

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in the system (x $PbCl_2$ + x CsCl) —— (1-2x) NaCl

| composition (m.f.$PbCl_2$) | activity $PbCl_2$ | | | activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | 600°C | 700°C | 800°C |
| 0.398 | 0.1473 | 0.1570 | 0.1648 | 0.3697 | 0.3941 | 0.4137 |
| 0.329 | 0.1335 | 0.1360 | 0.1385 | 0.4061 | 0.4138 | 0.4218 |
| 0.250 | 0.1048 | 0.1012 | 0.0984 | 0.4192 | 0.4048 | 0.3936 |
| 0.145 | 0.0815 | 0.0736 | 0.0678 | 0.5617 | 0.5072 | 0.4673 |

TABLE 3.39

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in the system (x $PbCl_2$ + x CsCl) —— (1-2x) KCl

| composition (m.f.$PbCl_2$) | activity $PbCl_2$ | | | activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | 600°C | 700°C | 800°C |
| 0.396 | 0.1207 | 0.1176 | 0.1152 | 0.3049 | 0.2970 | 0.2910 |
| 0.322 | 0.0556 | 0.0597 | 0.0635 | 0.1725 | 0.1852 | 0.1970 |
| 0.248 | 0.0310 | 0.0363 | 0.0400 | 0.1251 | 0.1465 | 0.1614 |

TABLE 3.40

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in the system (x $PbCl_2$ + x CsCl) —— (1-2x) RbCl

| composition (m.f.$PbCl_2$) | activity $PbCl_2$ | | | activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | 600°C | 700°C | 800°C |
| 0.396 | 0.0875 | 0.0908 | 0.0933 | 0.2209 | 0.2292 | 0.2355 |
| 0.322 | 0.0407 | 0.0442 | 0.0473 | 0.1265 | 0.1374 | 0.1470 |
| 0.250 | 0.0185 | 0.0225 | 0.0265 | 0.0741 | 0.0901 | 0.1062 |

TABLE 3.41

Partial molar thermodynamic functions of $PbCl_2$ in the system (x $PbCl_2$ + x CsCl) —— (1-2x)LiCl

| | | | | | |
|---|---|---|---|---|---|
| | | | 700°C | | |
| mole fraction $PbCl_2$ | 1.000 | 0.399 | 0.324 | 0.245 | 0.150 |
| $\Delta G_1$ (K cal/mole) | -53.14 | -55.96 | -56.41 | -56.66 | -56.97 |
| $\Delta S_1$ (cal/deg/mole) | -26.40 | -26.42 | -22.81 | -20.58 | -20.44 |
| $\Delta H_1$ (K cal/mole) | -78.82 | -81.66 | -78.60 | -76.69 | -76.86 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 2.82 | - 3.27 | - 3.52 | - 3.83 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | - 0.02 | + 3.59 | + 5.82 | + 5.96 |
| $\Delta \bar{H}_1$ (K cal/mole) | | - 2.84 | + 0.22 | + 2.14 | + 1.96 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 1.04 | - 1.09 | - 0.80 | - 0.16 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | - 1.85 | + 1.35 | + 3.02 | + 2.18 |
| | | | 600°C | | |
| $\Delta G_1$ (K cal/mole) | -55.78 | -58.61 | -58.69 | -58.72 | -59.02 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 2.83 | - 2.92 | - 2.94 | - 3.24 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 1.23 | - 0.96 | - 0.50 | + 0.06 |
| | | | 800°C | | |
| $\Delta G_1$ (K cal/mole) | -50.50 | -53.32 | -54.13 | -54.60 | -54.92 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 2.82 | - 3.63 | - 4.10 | - 4.42 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.85 | - 1.23 | - 1.09 | - 0.37 |

TABLE 3.40

Partial molar thermodynamic functions of $PbCl_2$ in the system (x $PbCl_2$ + x CsCl) —— (1-2x)NaCl

| | | | | | |
|---|---|---|---|---|---|
| | | | 700°C | | |
| mole fraction $PbCl_2$ | 1.000 | 0.398 | 0.329 | 0.250 | 0.145 |
| $\Delta G_1$ (K cal/mole) | -53.14 | -56.72 | -57.00 | -57.57 | -58.19 |
| $\Delta S_1$ (cal/deg/mole) | -26.40 | -23.77 | -22.75 | -21.23 | -19.43 |
| $\Delta H_1$ (K cal/mole) | -78.82 | -79.85 | -79.14 | -78.23 | -77.09 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 3.58 | - 3.86 | - 4.43 | - 5.05 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | + 2.63 | + 3.65 | + 5.17 | + 6.97 |
| $\Delta \bar{H}_1$ (K cal/mole) | | - 1.03 | - 0.31 | + 0.59 | + 1.73 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 1.80 | - 1.71 | - 1.75 | - 1.31 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | + 0.80 | + 1.44 | + 2.41 | + 3.13 |
| | | | 600°C | | |
| $\Delta G_1$ (K cal/mole) | -55.78 | -59.10 | -59.27 | -59.69 | -60.13 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 3.33 | - 3.50 | - 3.92 | - 4.35 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 1.73 | - 1.56 | - 1.51 | - 1.00 |
| | | | 800°C | | |
| $\Delta G_1$ (K cal/mole) | -50.50 | -54.35 | -54.72 | -55.45 | -56.24 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 3.85 | - 4.22 | - 4.95 | - 5.74 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 1.88 | - 1.84 | - 1.99 | - 1.62 |

TABLE 3.43

**Partial molar thermodynamic functions of $PbCl_2$ in the system (x $PbCl_2$ + x CsCl) —— (1-2x)KCl**

| | | | | |
|---|---|---|---|---|
| | | 700°C | | |
| mole fraction $PbCl_2$ | 1.000 | 0.396 | 0.322 | 0.248 |
| $\Delta G_1$ (K cal/mole) | -53.14 | -57.28 | -58.59 | -59.59 |
| $\Delta S_1$ (cal/deg/mole) | -26.40 | -21.67 | -22.08 | -22.21 |
| $\Delta H_1$ (K cal/mole) | -78.82 | -78.37 | -80.07 | -81.20 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 4.14 | - 5.45 | - 6.45 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | + 4.72 | + 4.32 | + 4.19 |
| $\Delta \bar{H}_1$ (K cal/mole) | | + 0.45 | - 1.25 | - 2.38 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 2.35 | - 3.26 | - 3.71 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | + 2.88 | + 2.07 | + 1.42 |
| | | 600°C | | |
| $\Delta G_1$ (K cal/mole) | -55.78 | -59.45 | -60.80 | -61.81 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 3.67 | - 5.02 | - 6.03 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 2.06 | - 3.05 | - 3.61 |
| | | 800°C | | |
| $\Delta G_1$ (K cal/mole) | -50.50 | -55.11 | -56.38 | -57.37 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 4.61 | - 5.88 | - 6.87 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 2.63 | - 3.46 | - 3.89 |

TABLE 3.44

Partial molar thermodynamic functions of $PbCl_2$ in the system (x $PbCl_2$ + x CsCl) —— (1-2x)RbCl

| | | | | |
|---|---|---|---|---|
| | | 700°C | | |
| mole fraction $PbCl_2$ | 1.000 | 0.396 | 0.322 | 0.250 |
| $\Delta G_1$ (K cal/mole) | -53.14 | -57.78 | -59.18 | -60.48 |
| $\Delta S_1$ (cal/deg/mole) | -26.40 | -22.22 | -21.60 | -22.26 |
| $\Delta H_1$ (K cal/mole) | -78.82 | -79.40 | -80.19 | -82.14 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 4.65 | - 6.04 | - 7.34 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | + 4.18 | + 4.80 | + 4.13 |
| $\Delta \bar{H}_1$ (K cal/mole) | | - 0.58 | - 1.37 | - 3.32 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 2.85 | - 3.84 | - 4.65 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | + 2.34 | + 2.55 | + 1.38 |
| | | 600°C | | |
| $\Delta G_1$ (K cal/mole) | -55.78 | -60.01 | -61.34 | -62.71 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 4.23 | - 5.56 | - 6.93 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 2.62 | - 3.59 | - 4.52 |
| | | 800°C | | |
| $\Delta G_1$ (K cal/mole) | -50.50 | -55.56 | -57.01 | -58.25 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 5.06 | - 6.51 | - 7.75 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 3.08 | - 4.09 | - 4.78 |

## TABLE 3.45

**Differences in the partial molar free energies ( $\Delta\bar{G}_1$*(MCl) of $PbCl_2$ in the systems $PbCl_2$-CsCl and (x $PbCl_2$ + x CsCl) —— (1-2x)MCl as functions of the ratio (m.f.MCl)/(m.f.CsCl) at 700°C**

| composition (m.f.$PbCl_2$) | $\frac{N_{MCl}}{N_{CsCl}}$ | $\Delta\bar{G}_1$*(LiCl) | $\Delta\bar{G}_1$*(NaCl) | $\Delta\bar{G}_1$*(KCl) | $\Delta\bar{G}_1$*(RbCl) |
|---|---|---|---|---|---|
| 0.50 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.45 | 0.222 ± 0.03 | +1.10 | +0.50 | +0.38 | +0.10 |
| 0.40 | 0.500 ± 0.05 | +1.97 | +1.22 | +0.70 | +0.22 |
| 0.35 | 0.857 ± 0.05 | +2.63 | +2.02 | +0.86 | +0.29 |
| 0.30 | 1.333 ± 0.08 | +3.53 | +2.80 | +1.11 | +0.47 |
| 0.25 | 2.000 ± 0.14 | +4.75 | +3.82 | +1.82 | +0.90 |

Errors arise in $\frac{N_{MCl}}{N_{CsCl}}$ because of the uncertainty in the ratio $\frac{N_{PbCl_2}}{N_{CsCl}}$ (= x)

Experimentally x is not always equal to 1.

TABLE 3.46

Values of e.m.f. and temperature for the formation cells:

$Pb/(2x\ PbCl_2 + x\ CsCl) \rightarrow (1-3x)\ LiCl/C, Cl_2$

| composition (m.f. $PbCl_2$) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) | temp. (°C) | e.m.f. (volts) | ΔE (mv.) |
|---|---|---|---|---|---|---|
| 0.551 | 636.0 | 1.2170 | -0.5 | 744.9 | 1.1674 | -0.4 |
| | 663.0 | 1.2050 | -0.1 | 770.3 | 1.1561 | -0.1 |
| | 686.8 | 1.1947 | +0.4 | 797.2 | 1.1439 | 0.0 |
| | 712.2 | 1.1832 | +0.5 | 821.0 | 1.1333 | +0.2 |
| 0.491 | 618.0 | 1.2315 | -0.7 | 729.8 | 1.1770 | +0.7 |
| | 646.1 | 1.2182 | 0.0 | 721.3 | 1.1807 | +0.2 |
| | 672.0 | 1.2051 | -0.1 | 749.1 | 1.1664 | -0.2 |
| | 698.0 | 1.1922 | 0.0 | 777.3 | 1.1524 | -0.1 |
| 0.418 | 626.0 | 1.2337 | +0.4 | 733.0 | 1.1806 | 0.0 |
| | 650.2 | 1.2210 | -0.3 | 760.1 | 1.1671 | -0.1 |
| | 678.8 | 1.2074 | +0.1 | 789.2 | 1.1528 | -0.1 |
| | 705.8 | 1.1936 | -0.4 | 810.0 | 1.1428 | +0.2 |
| 0.322 | 640.6 | 1.2268 | +0.4 | 749.0 | 1.1743 | 0.0 |
| | 667.4 | 1.2134 | -0.1 | 771.2 | 1.1636 | 0.0 |
| | 692.8 | 1.2010 | -0.3 | 805.1 | 1.1475 | +0.2 |
| | 722.0 | 1.1872 | -0.1 | 821.3 | 1.1391 | -0.4 |
| 0.250 | 653.0 | 1.2273 | -0.1 | 759.0 | 1.1803 | +0.5 |
| | 679.2 | 1.2158 | +0.2 | 787.2 | 1.1672 | 0.0 |
| | 706.0 | 1.2029 | -0.7 | 807.1 | 1.1580 | -0.3 |
| | 732.1 | 1.1921 | +0.2 | 830.0 | 1.1480 | 0.0 |

TABLE 3.47

**Values of e.m.f. and temperature for the formation cells:**

**$Pb/(2x\ PbCl_2 + x\ CsCl)$ —— $(1-3x)\ NaCl/C, Cl_2$**

| composition (m.f.$PbCl_2$) | temp. (°C) | e.m.f. (volts) | $\triangle E$ (mv.) | temp. (°C) | e.m.f. (volts) | $\triangle E$ (mv.) |
|---|---|---|---|---|---|---|
| 0.561 | 636.8 | 1.2233 | +0.4 | 734.0 | 1.1686 | -0.2 |
| | 662.4 | 1.2094 | +0.8 | 759.8 | 1.1556 | +1.1 |
| | 686.0 | 1.1948 | -0.7 | 782.1 | 1.1420 | -0.1 |
| | 709.2 | 1.1816 | -1.0 | 799.8 | 1.1325 | +0.3 |
| 0.461 | 652.8 | 1.2237 | -1.1 | 753.0 | 1.1765 | +0.6 |
| | 679.0 | 1.2120 | 0.0 | 776.4 | 1.1645 | 0.0 |
| | 704.8 | 1.1998 | +0.4 | 805.1 | 1.1502 | -0.3 |
| | 729.4 | 1.1875 | +0.1 | 830.2 | 1.1382 | -0.1 |
| 0.355 | 683.5 | 1.2130 | -0.4 | 783.0 | 1.1653 | -0.2 |
| | 708.7 | 1.2018 | +0.5 | 806.8 | 1.1536 | -0.5 |
| | 732.4 | 1.1903 | +0.4 | 831.2 | 1.1424 | +0.1 |
| | 759.0 | 1.1770 | -0.1 | 855.5 | 1.1303 | -0.3 |
| 0.237 | 748.6 | 1.2032 | 0.0 | 823.2 | 1.1678 | -0.1 |
| | 773.0 | 1.1911 | -0.5 | 848.0 | 1.1568 | +0.7 |
| | 796.5 | 1.1804 | -0.1 | 862.1 | 1.1495 | 0.0 |

TABLE 3.48

Values of e.m.f. and temperature for the formation cells:

$Pb/(2x\ PbCl_2 + x\ CsCl)$ —— $(1-3x)\ KCl/C, Cl_2$

| composition (m.f.$PbCl_2$) | temp. ($^oC$) | e.m.f. (volts) | $\Delta E$ (mv.) | temp. ($^oC$) | e.m.f. (volts) | $\Delta E$ (mv.) |
|---|---|---|---|---|---|---|
| 0.501 | 644.0 | 1.2382 | -0.2 | 752.0 | 1.1851 | +0.3 |
| | 673.0 | 1.2239 | -0.1 | 775.4 | 1.1729 | -0.3 |
| | 697.2 | 1.2119 | -0.1 | 799.2 | 1.1614 | 0.0 |
| | 723.6 | 1.1990 | +0.1 | | | |
| 0.407 | 628.4 | 1.2714 | 0.0 | 733.4 | 1.2205 | +0.6 |
| | 655.0 | 1.2580 | -0.4 | 760.2 | 1.2065 | -0.3 |
| | 680.0 | 1.2460 | -0.1 | 787.9 | 1.1932 | 0.0 |
| | 707.5 | 1.2330 | +0.4 | 810.1 | 1.1825 | +0.2 |
| 0.330 | 652.6 | 1.2785 | 0.0 | 755.2 | 1.2295 | 0.0 |
| | 679.2 | 1.2655 | -0.3 | 781.8 | 1.2164 | -0.4 |
| | 704.0 | 1.2542 | +0.2 | 805.7 | 1.2055 | +0.1 |
| | 729.0 | 1.2424 | +0.4 | 829.9 | 1.1936 | -0.2 |
| 0.241 | 685.8 | 1.2915 | +0.3 | 763.4 | 1.2556 | +0.3 |
| | 712.2 | 1.2788 | -0.2 | 789.1 | 1.2435 | +0.1 |
| | 737.0 | 1.2670 | -0.5 | 815.7 | 1.2310 | -0.1 |

TABLE 3.49

Values of e.m.f. and temperature for the formation cells:

$Pb/(2x\ PbCl_2 + x\ CsCl) \text{ —— } (1-3x)\ RbCl/C,\ Cl_2$

| composition (m.f.$PbCl_2$) | temp. (°C) | e.m.f. (volts) | $\Delta E$ (mv.) | temp. (°C) | e.m.f. (volts) | $\Delta E$ (mv.) |
|---|---|---|---|---|---|---|
| 0.594 | 627.0 | 1.2288 | 0.0 | 735.8 | 1.1765 | +0.6 |
| | 653.0 | 1.2158 | -0.3 | 760.1 | 1.1641 | 0.0 |
| | 679.0 | 1.2028 | -0.7 | 789.2 | 1.1497 | -0.2 |
| | 707.5 | 1.1899 | +0.3 | 817.1 | 1.1360 | -0.3 |
| 0.524 | 649.0 | 1.2352 | -0.8 | 757.4 | 1.1825 | +1.3 |
| | 677.7 | 1.2212 | -0.3 | 783.2 | 1.1682 | 0.0 |
| | 705.6 | 1.2070 | -0.4 | 808.7 | 1.1552 | -0.1 |
| | 732.7 | 1.1940 | +0.3 | | | |
| 0.444 | 648.0 | 1.2601 | +0.2 | 755.8 | 1.2089 | +0.2 |
| | 675.0 | 1.2470 | +0.4 | 780.1 | 1.1971 | 0.0 |
| | 703.2 | 1.2342 | -0.3 | 819.0 | 1.1782 | -0.3 |
| | 729.2 | 1.2216 | +0.1 | 840.2 | 1.1682 | -0.1 |
| 0.374 | 637.0 | 1.2894 | 0.0 | 745.2 | 1.2372 | +0.1 |
| | 666.0 | 1.2754 | 0.0 | 771.3 | 1.2240 | -0.1 |
| | 693.0 | 1.2622 | -0.2 | 795.2 | 1.2133 | +0.3 |
| | 719.5 | 1.2497 | +0.1 | 819.9 | 1.2009 | -0.2 |
| 0.278 | 643.0 | 1.3237 | -0.3 | 747.4 | 1.2745 | -0.2 |
| | 669.8 | 1.3114 | +0.1 | 771.7 | 1.2632 | 0.0 |
| | 694.6 | 1.2997 | +0.1 | 798.1 | 1.2506 | -0.1 |
| | 722.6 | 1.2865 | +0.1 | | | |

TABLE 3.50

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:

Pb/(2x $PbCl_2$ + x CsCl) —— (1-3x) LiCl/C, $Cl_2$

| composition | | | e.m.f. at temperature t°C (volts) | mean deviation mV |
|---|---|---|---|---|
| m.f.$PbCl_2$ | m.f.CsCl | m.f.LiCl | | |
| 0.551 | 0.281 | 0.168 | $1.5076 - (4.562 \times 10^{-4})t$ | 0.3 |
| 0.491 | 0.260 | 0.249 | $1.5414 - (5.003 \times 10^{-4})t$ | 0.3 |
| 0.418 | 0.205 | 0.377 | $1.5417 - (4.927 \times 10^{-4})t$ | 0.2 |
| 0.322 | 0.169 | 0.510 | $1.5341 - (4.804 \times 10^{-4})t$ | 0.2 |
| 0.250 | 0.122 | 0.628 | $1.5201 - (4.483 \times 10^{-4})t$ | 0.2 |

TABLE 3.51

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:

Pb/(2x $PbCl_2$ + x CsCl) —— (1-3x) NaCl/C, $Cl_2$

| composition | | | e.m.f. at temperature t°C (volts) | mean deviation mV |
|---|---|---|---|---|
| m.f.$PbCl_2$ | m.f.CsCl | m.f.NaCl | | |
| 0.561 | 0.293 | 0.147 | $1.5770 - (5.561 \times 10^{-4})t$ | 0.6 |
| 0.461 | 0.234 | 0.305 | $1.5431 - (4.876 \times 10^{-4})t$ | 0.3 |
| 0.355 | 0.170 | 0.475 | $1.5423 - (4.812 \times 10^{-4})t$ | 0.3 |
| 0.237 | 0.122 | 0.641 | $1.5574 - (4.732 \times 10^{-4})t$ | 0.2 |

## TABLE 3.52

**Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:**

**$Pb/(2x\ PbCl_2 + x\ CsCl) \text{ —— } (1-3x)\ KCl/\ C, Cl_2$**

| composition | | | e.m.f. at temperature t°C (volts) | mean deviation (mV) |
|---|---|---|---|---|
| m.f.$PbCl_2$ | m.f.CsCl | m.f.KCl | | |
| 0.501 | 0.254 | 0.245 | $1.5576 - (4.957 \times 10^{-4})t$ | 0.2 |
| 0.407 | 0.212 | 0.381 | $1.5795 - (4.903 \times 10^{-4})t$ | 0.2 |
| 0.330 | 0.164 | 0.506 | $1.5904 - (4.779 \times 10^{-4})t$ | 0.2 |
| 0.241 | 0.122 | 0.637 | $1.6084 - (4.625 \times 10^{-4})t$ | 0.3 |

## TABLE 3.53

**Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:**

**$Pb/(2x\ PbCl_2 + x\ CsCl) \text{ —— } (1-3x)\ RbCl/C, Cl_2$**

| composition | | | e.m.f. at temperature t°C (volts) | mean deviation (mV) |
|---|---|---|---|---|
| m.f.$PbCl_2$ | m.f.CsCl | m.f.RbCl | | |
| 0.594 | 0.320 | 0.086 | $1.5337 - (4.863 \times 10^{-4})t$ | 0.3 |
| 0.524 | 0.254 | 0.222 | $1.5641 - (5.055 \times 10^{-4})t$ | 0.4 |
| 0.444 | 0.232 | 0.324 | $1.5706 - (4.788 \times 10^{-4})t$ | 0.2 |
| 0.374 | 0.195 | 0.430 | $1.5970 - (4.829 \times 10^{-4})t$ | 0.2 |
| 0.278 | 0.133 | 0.590 | $1.6276 - (4.722 \times 10^{-4})t$ | 0.1 |

TABLE 3.54

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in the system:

$(2x\ PbCl_2 + x\ CsCl)$ —— $(1-3x)\ LiCl$

| composition (m.f.$PbCl_2$) | activity $PbCl_2$ | | | activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | 600°C | 700°C | 800°C |
| 0.551 | 0.5202 | 0.4220 | 0.3567 | 0.9436 | 0.7655 | 0.6470 |
| 0.491 | 0.4285 | 0.3938 | 0.3676 | 0.8722 | 0.8015 | 0.7482 |
| 0.418 | 0.3762 | 0.3445 | 0.3207 | 0.9006 | 0.8248 | 0.7678 |
| 0.322 | 0.3782 | 0.3364 | 0.3053 | 1.1756 | 1.0457 | 0.9490 |
| 0.250 | 0.3295 | 0.2748 | 0.2370 | 1.3180 | 1.0992 | 0.9480 |

TABLE 3.55

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in the system:

$(2x\ PbCl_2 + x\ CsCl)$ —— $(1-3x)\ NaCl$

| composition (m.f.$PbCl_2$) | activity $PbCl_2$ | | | activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | 600°C | 700°C | 800°C |
| 0.561 | 0.4053 | 0.4282 | 0.4476 | 0.7225 | 0.7633 | 0.7979 |
| 0.461 | 0.3347 | 0.3059 | 0.2848 | 0.7260 | 0.6636 | 0.6178 |
| 0.355 | 0.3082 | 0.2801 | 0.2596 | 0.8679 | 0.7888 | 0.7311 |
| 0.237 | 0.1818 | 0.1710 | 0.1673 | 0.7671 | 0.7215 | 0.7059 |

TABLE 3.56

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in the system:

$(2x\ PbCl_2 + x\ CsCl)$ —— $(1-3x)\ KCl$

| composition (m.f.$PbCl_2$) | activity $PbCl_2$ | | | activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | 600°C | 700°C | 800°C |
| 0.501 | 0.2587 | 0.2479 | 0.2396 | 0.5166 | 0.4950 | 0.4784 |
| 0.407 | 0.1328 | 0.1344 | 0.1357 | 0.3260 | 0.3299 | 0.3331 |
| 0.330 | 0.0815 | 0.0843 | 0.0865 | 0.2471 | 0.2556 | 0.2623 |
| 0.241 | 0.0395 | 0.0425 | 0.0450 | 0.1638 | 0.1763 | 0.1866 |

TABLE 3.57

Value of the activity and activity coefficient of $PbCl_2$ at different compositions in the system:

$(2x\ PbCl_2 + x\ CsCl)$ —— $(1-3x)\ RbCl$

| composition (m.f.$PbCl_2$) | activity $PbCl_2$ | | | activity coeff. $PbCl_2$ | | |
|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | 600°C | 700°C | 800°C |
| 0.594 | 0.4207 | 0.3745 | 0.3409 | 0.7082 | 0.6305 | 0.5739 |
| 0.524 | 0.2546 | 0.2503 | 0.2465 | 0.4857 | 0.4775 | 0.4702 |
| 0.444 | 0.1401 | 0.1374 | 0.1348 | 0.3156 | 0.3095 | 0.3037 |
| 0.374 | 0.0740 | 0.0782 | 0.0820 | 0.1976 | 0.2089 | 0.2190 |
| 0.278 | 0.0277 | 0.0316 | 0.0352 | 0.0998 | 0.1138 | 0.1268 |

## TABLE 3.58

**Partial molar thermodynamic functions of $PbCl_2$ in the system:**

**$(2x\ PbCl_2 + x\ CsCl) \rightleftharpoons (1-3x)\ LiCl$**

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | 700°C | | |
| mole fraction $PbCl_2$ | 1.000 | 0.551 | 0.491 | 0.418 | 0.322 | 0.250 |
| $\Delta G_1$ (K cal/mole) | -53.14 | -54.81 | -54.94 | -55.20 | -55.25 | -55.64 |
| $\Delta S_1$ (cal/deg/mole) | -26.40 | -21.04 | -23.08 | -22.73 | -22.16 | -20.68 |
| $\Delta H_1$ (K cal/mole) | -78.82 | -75.28 | -77.40 | -77.33 | -76.81 | -75.76 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 1.67 | - 1.80 | - 2.06 | - 2.11 | - 2.50 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | + 5.36 | + 3.32 | + 3.67 | + 4.24 | + 5.72 |
| $\Delta \bar{H}_1$ (K cal/mole) | | + 3.54 | + 1.43 | + 1.49 | + 2.02 | + 3.06 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.52 | - 0.43 | - 0.37 | + 0.09 | + 0.18 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | + 4.17 | + 1.91 | + 1.94 | + 1.99 | + 2.97 |
| | | | | 600°C | | |
| $\Delta G_1$ (K cal/mole) | -55.78 | -56.91 | -57.25 | -57.48 | -57.47 | -57.71 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 1.13 | - 1.47 | - 1.70 | - 1.69 | - 1.93 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.10 | - 0.24 | - 0.18 | + 0.28 | + 0.48 |
| | | | | 800°C | | |
| $\Delta G_1$ (K cal/mole) | -50.50 | -52.70 | -52.64 | -52.93 | -53.03 | -53.57 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 2.20 | - 2.14 | - 2.43 | - 2.53 | - 3.07 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.93 | - 0.62 | - 0.56 | - 0.11 | - 0.11 |

## TABLE 3.59

**Partial molar thermodynamic functions of $PbCl_2$ in the system:**

**$(2x\ PbCl_2 + x\ CsCl)$ —— $(1-3x)$ NaCl**

| | | | | | |
|---|---|---|---|---|---|
| | | | 700°C | | |
| mole fraction $PbCl_2$ | 1.000 | 0.561 | 0.461 | 0.355 | 0.237 |
| $\Delta G_1$ (K cal/mole) | -53.14 | -54.78 | -55.43 | -55.60 | -56.56 |
| $\Delta S_1$ (cal/deg/mole) | -26.40 | -25.65 | -22.49 | -22.20 | -21.83 |
| $\Delta H_1$ (K cal/mole) | -78.82 | -79.74 | -77.31 | -77.20 | -77.79 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 1.64 | - 2.29 | - 2.46 | - 3.42 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | - 0.75 | + 3.91 | + 4.20 | + 4.57 |
| $\Delta \bar{H}_1$ (K cal/mole) | | - 0.92 | + 1.51 | + 1.62 | + 1.03 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.52 | - 0.79 | - 0.46 | - 0.63 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | - 0.40 | + 2.37 | + 2.14 | + 1.71 |
| | | | 600°C | | |
| $\Delta G_1$ (K cal/mole) | -55.78 | -57.35 | -57.68 | -57.82 | -58.74 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 1.57 | - 1.90 | - 2.04 | - 2.96 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.56 | - 0.56 | - 0.25 | - 0.46 |
| | | | 800°C | | |
| $\Delta G_1$ (K cal/mole) | -50.50 | -52.22 | -53.18 | -53.38 | -54.37 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 1.72 | - 2.68 | - 2.88 | - 3.87 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 0.48 | - 1.03 | - 0.67 | - 0.74 |

## TABLE 3.60

### Partial molar thermodynamic functions of $PbCl_2$ in the system:

### $(2x\ PbCl_2 + x\ CsCl) \rightleftharpoons (1-3x)\ KCl$

| | | | | | |
|---|---|---|---|---|---|
| | | | 700°C | | |
| mole fraction $PbCl_2$ | 1.000 | 0.501 | 0.407 | 0.330 | 0.241 |
| $\Delta G_1$ (K cal/mole) | -53.14 | -55.84 | -57.02 | -57.93 | -59.25 |
| $\Delta S_1$ (cal/deg/mole) | -26.40 | -22.86 | -22.62 | -22.04 | -21.33 |
| $\Delta H_1$ (K cal/mole) | -78.82 | -78.08 | -79.03 | -79.38 | -80.01 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 2.70 | - 3.88 | - 4.79 | - 6.11 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | + 3.53 | + 3.78 | + 4.35 | + 5.07 |
| $\Delta \bar{H}_1$ (K cal/mole) | | + 0.74 | - 0.21 | - 0.55 | - 1.19 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 1.36 | - 2.14 | - 2.64 | - 3.36 |
| $\Delta \bar{S}_1^E$ (cal/deg/mole) | | + 2.16 | + 2.00 | + 2.15 | + 2.24 |
| | | | 600°C | | |
| $\Delta G_1$ (K cal/mole) | -55.78 | -58.13 | -59.28 | -60.13 | -61.39 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 2.35 | - 3.51 | - 4.35 | - 5.61 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 1.15 | - 1.94 | - 2.43 | - 3.14 |
| | | | 800°C | | |
| $\Delta G_1$ (K cal/mole) | -50.50 | -53.55 | -54.76 | -55.72 | -57.12 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 3.05 | - 4.26 | - 5.22 | - 6.62 |
| $\Delta \bar{G}_1^E$ (K cal/mole) | | - 1.57 | - 2.34 | - 2.85 | - 3.58 |

## TABLE 3.61

### Partial molar thermodynamic functions of $PbCl_2$ in the system:

### $(2x\ PbCl_2 + x\ CsCl) \rightleftharpoons (1-3x)\ RbCl$

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | 700°C | | |
| mole fraction $PbCl_2$ | | 1.000 | 0.594 | 0.524 | 0.444 | 0.374 | 0.278 |
| $\Delta G_1$ | (K cal/mole) | -53.14 | -55.04 | -55.82 | -56.98 | -58.07 | -59.83 |
| $\Delta S_1$ | (cal/deg/mole) | -26.40 | -22.43 | -23.32 | -22.08 | -22.27 | -21.78 |
| $\Delta H_1$ | (K cal/mole) | -78.82 | -76.87 | -78.51 | -78.47 | -79.74 | -81.02 |
| $\Delta \bar{G}_1$ | (K cal/mole) | | - 1.90 | - 2.68 | - 3.84 | - 4.93 | - 6.69 |
| $\Delta \bar{S}_1$ | (cal/deg/mole) | | + 3.97 | + 3.08 | + 4.31 | + 4.12 | + 4.62 |
| $\Delta \bar{H}_1$ | (K cal/mole) | | + 1.96 | + 0.31 | + 0.35 | - 0.92 | - 2.20 |
| $\Delta \bar{G}_1^E$ | (K cal/mole) | | - 0.89 | - 1.43 | - 2.27 | - 3.03 | - 4.20 |
| $\Delta \bar{S}_1^E$ | (cal/deg/mole) | | + 2.93 | + 1.80 | + 2.70 | + 2.17 | + 2.07 |
| | | | | 600°C | | |
| $\Delta G_1$ | (K cal/mole) | -55.78 | -57.28 | -58.15 | -59.19 | -60.30 | -62.00 |
| $\Delta \bar{G}_1$ | (K cal/mole) | | - 1.50 | - 2.38 | - 3.41 | - 4.52 | - 6.23 |
| $\Delta \bar{G}_1^E$ | (K cal/mole) | | - 0.60 | - 1.25 | - 2.00 | - 2.81 | - 4.00 |
| | | | | 800°C | | |
| $\Delta G_1$ | (K cal/mole) | -50.50 | -52.80 | -53.49 | -54.78 | -55.84 | -57.65 |
| $\Delta \bar{G}_1$ | (K cal/mole) | | - 2.30 | - 2.99 | - 4.28 | - 5.34 | - 7.15 |
| $\Delta \bar{G}_1^E$ | (K cal/mole) | | - 1.18 | - 1.61 | - 2.54 | - 3.24 | - 4.40 |

TABLE 3.62

Differences in the partial molar free energies ( $\Delta\bar{G}_1$*(MCl) of $PbCl_2$ in the systems $PbCl_2$-CsCl and (2x $PbCl_2$ + x CsCl) —— (1-3x)MCl as functions of the ratio (m.f.MCl)/(m.f.CsCl) at 700°C

| composition (m.f.$PbCl_2$) | $\frac{N_{MCl}}{N_{CsCl}}$ | $\Delta\bar{G}_1$*(LiCl) | $\Delta\bar{G}_1$*(NaCl) | $\Delta\bar{G}_1$*(KCl) | $\Delta\bar{G}_1$*(RbCl) |
|---|---|---|---|---|---|
| 0.667 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.65 | 0.077 ± 0.04 | 0.14 | 0.13 | 0.05 | 0.03 |
| 0.60 | 0.333 ± 0.05 | 0.50 | 0.47 | 0.17 | 0.10 |
| 0.55 | 0.636 ± 0.07 | 0.82 | 0.79 | 0.29 | 0.12 |
| 0.50 | 1.000 ± 0.09 | 1.26 | 1.03 | 0.37 | 0.08 |
| 0.45 | 1.444 ± 0.12 | 1.92 | 1.55 | 0.55 | 0.15 |
| 0.40 | 2.000 ± 0.18 | 2.72 | 2.37 | 0.84 | 0.29 |
| 0.35 | 2.714 ± 0.25 | 3.70 | 3.26 | 1.22 | 0.63 |
| 0.30 | 3.667 ± 0.36 | 4.69 | 4.04 | 1.70 | 0.63 |
| 0.25 | 5.000 ± 0.55 | 5.75 | 5.00 | 2.30 | 0.87 |

Errors arise in $\frac{N_{MCl}}{N_{CsCl}}$ because of the uncertainty in the ratio $\frac{N_{PbCl_2}}{N_{CsCl}}$ (= x)

Experimentally x is not always equal to 2.

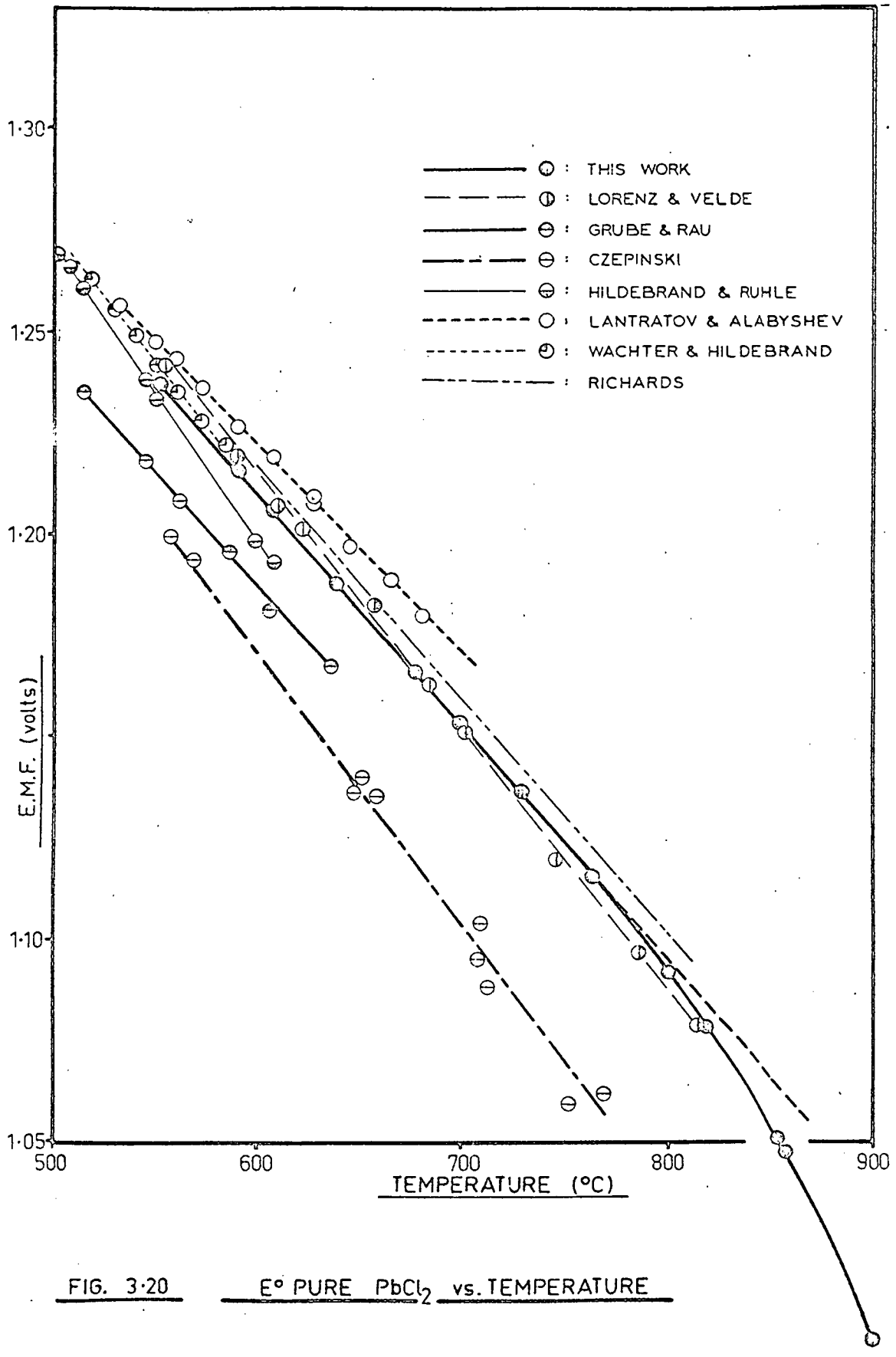



FIG. 3·20 E° PURE $PbCl_2$ vs. TEMPERATURE

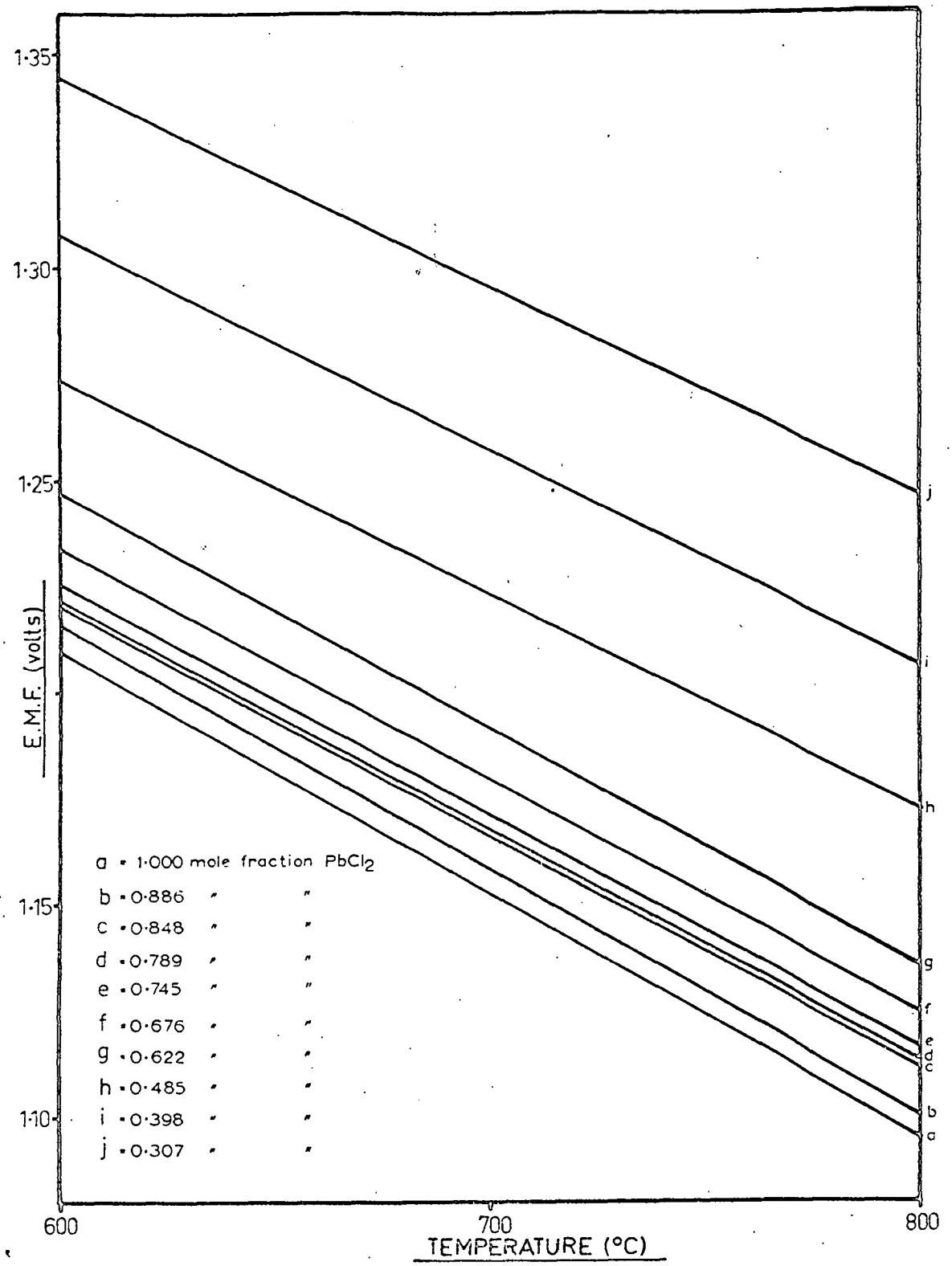



FIG. 3·21

SYSTEM $PbCl_2$-CsCl

E.M.F. vs. TEMPERATURE

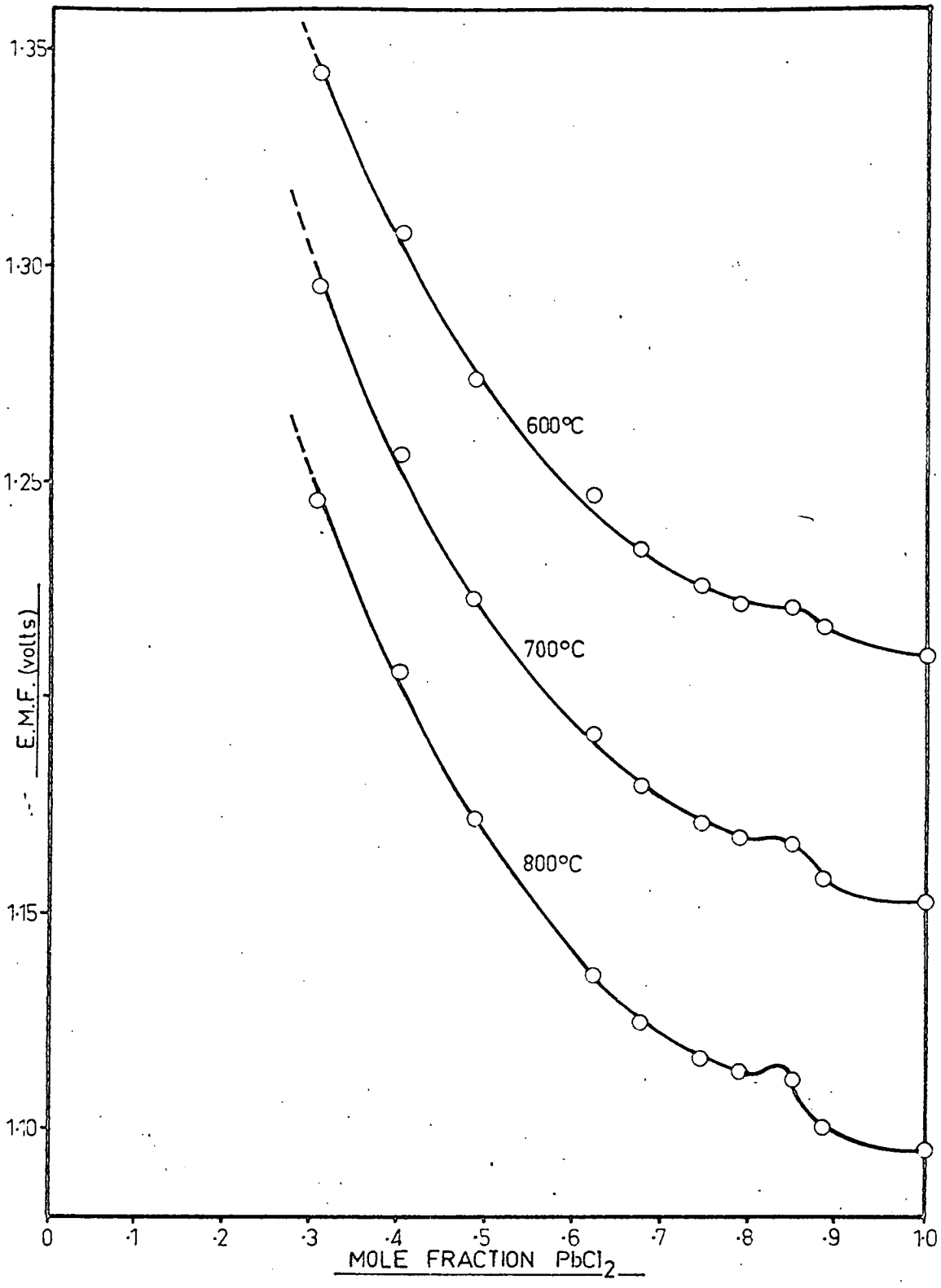



FIG. 3·22

SYSTEM $PbCl_2$–CsCl
E.M.F. vs. COMPOSITION

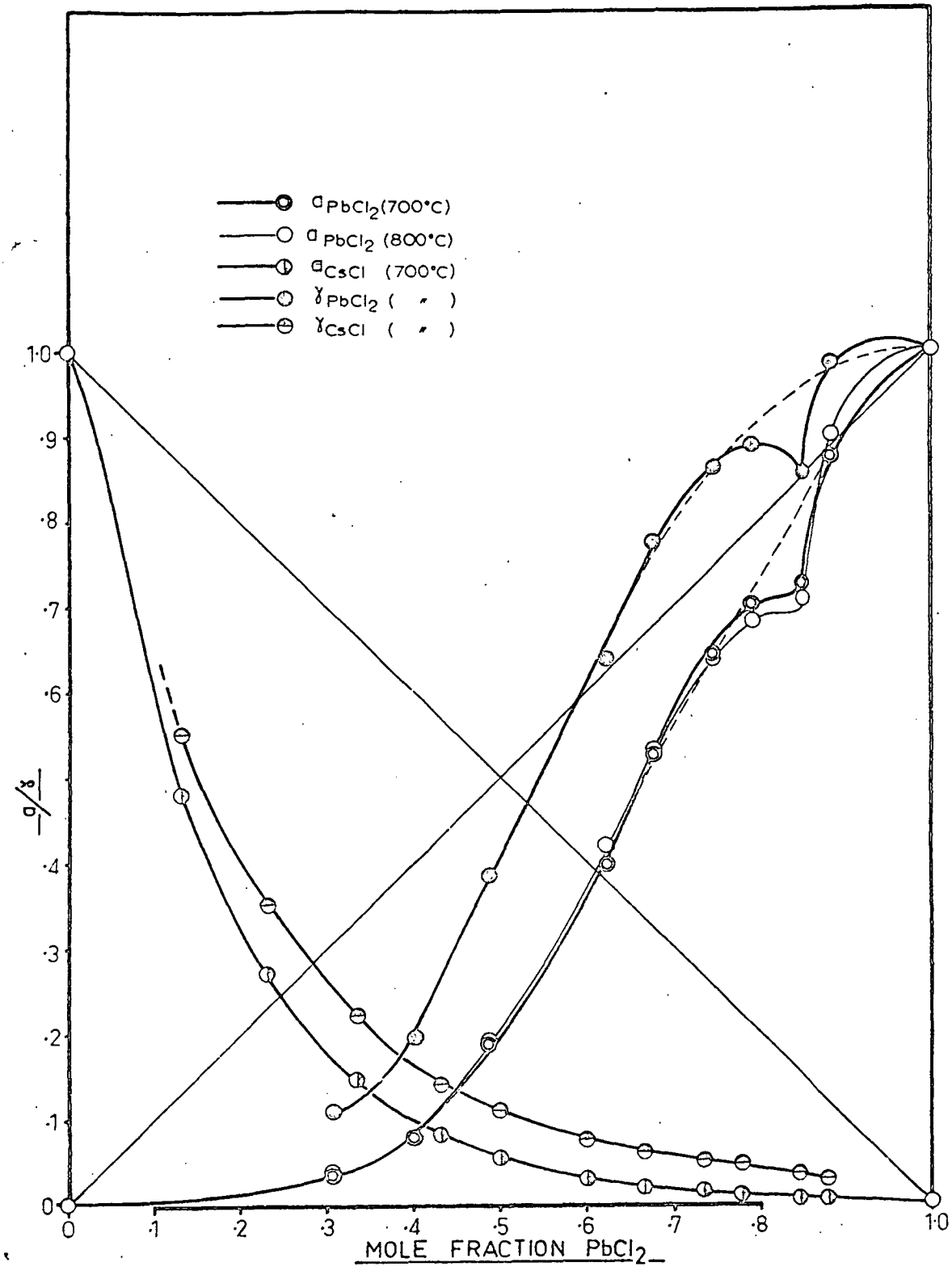



FIG. 3·23

SYSTEM $PbCl_2$-CsCl

ACTIVITIES & ACTIVITY COEFFS. vs COMPOSITION

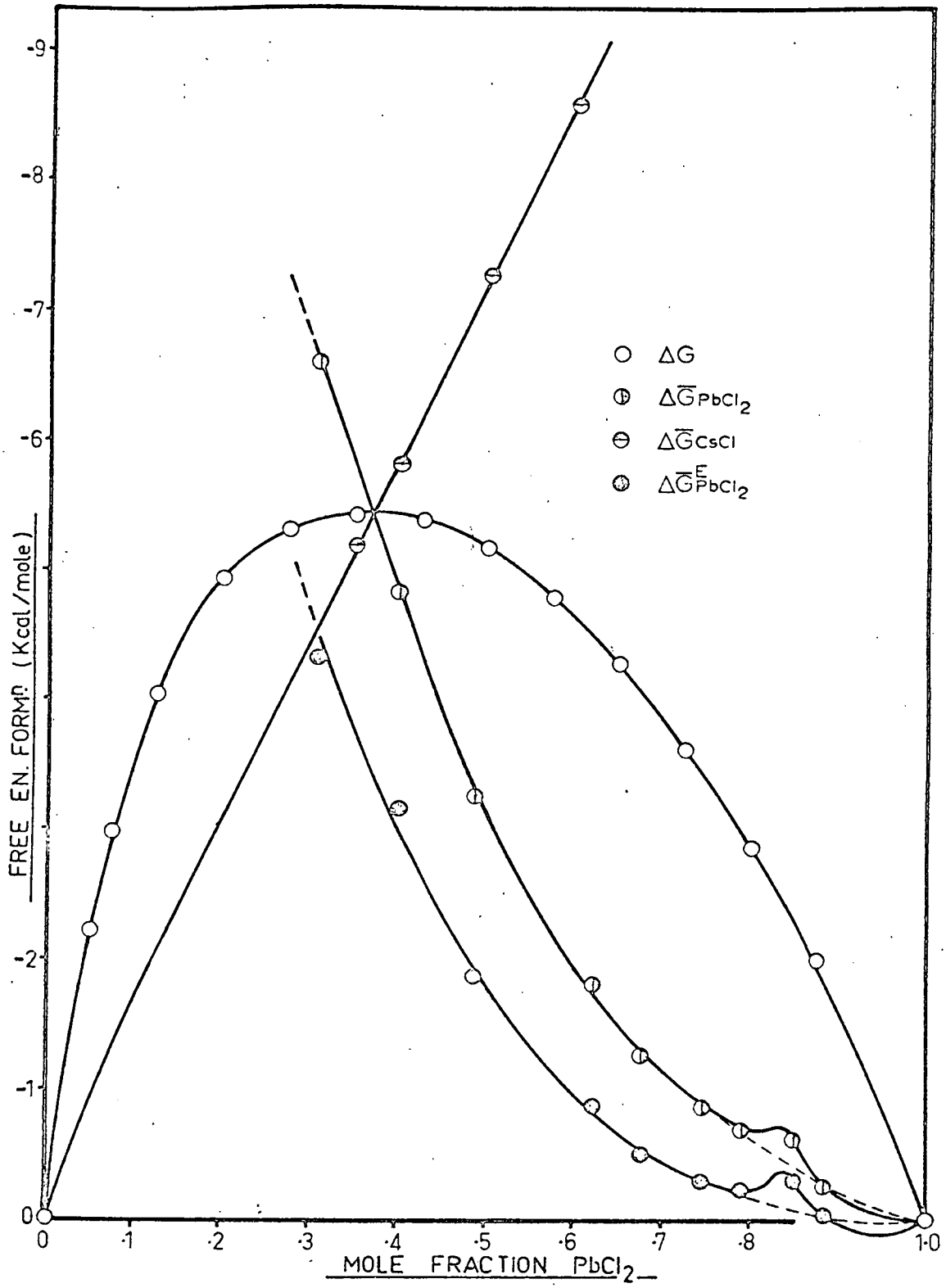



FIG. 3·24

SYSTEM $PbCl_2$-CsCl (700°C)

PARTIAL, INTEG., & EXCESS FREE ENERGIES vs COMPOSⁿ

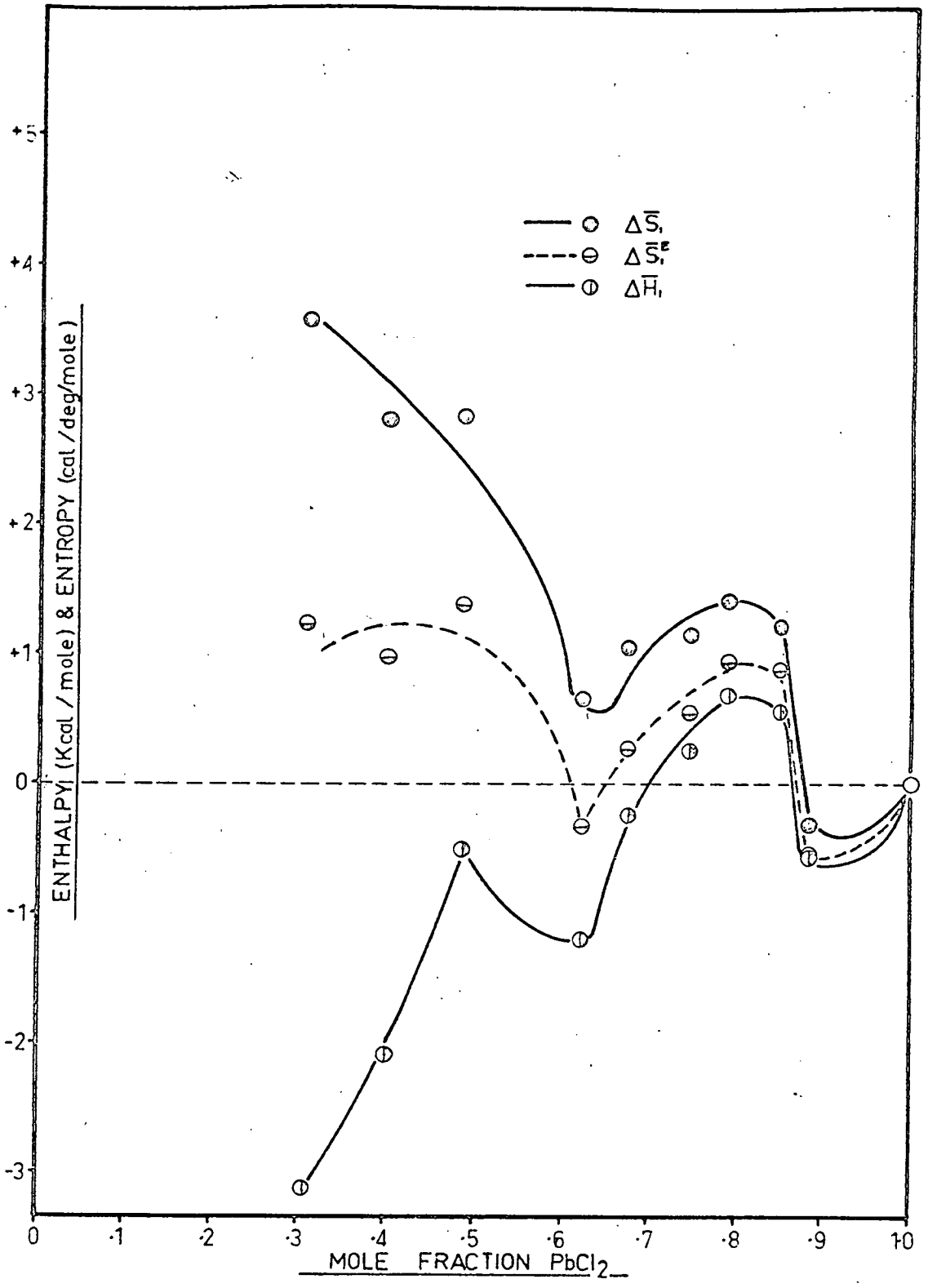



FIG. 3·25 SYSTEM $PbCl_2$–CsCl

PARTIAL THERMODYNAMIC FUNCTIONS $PbCl_2$

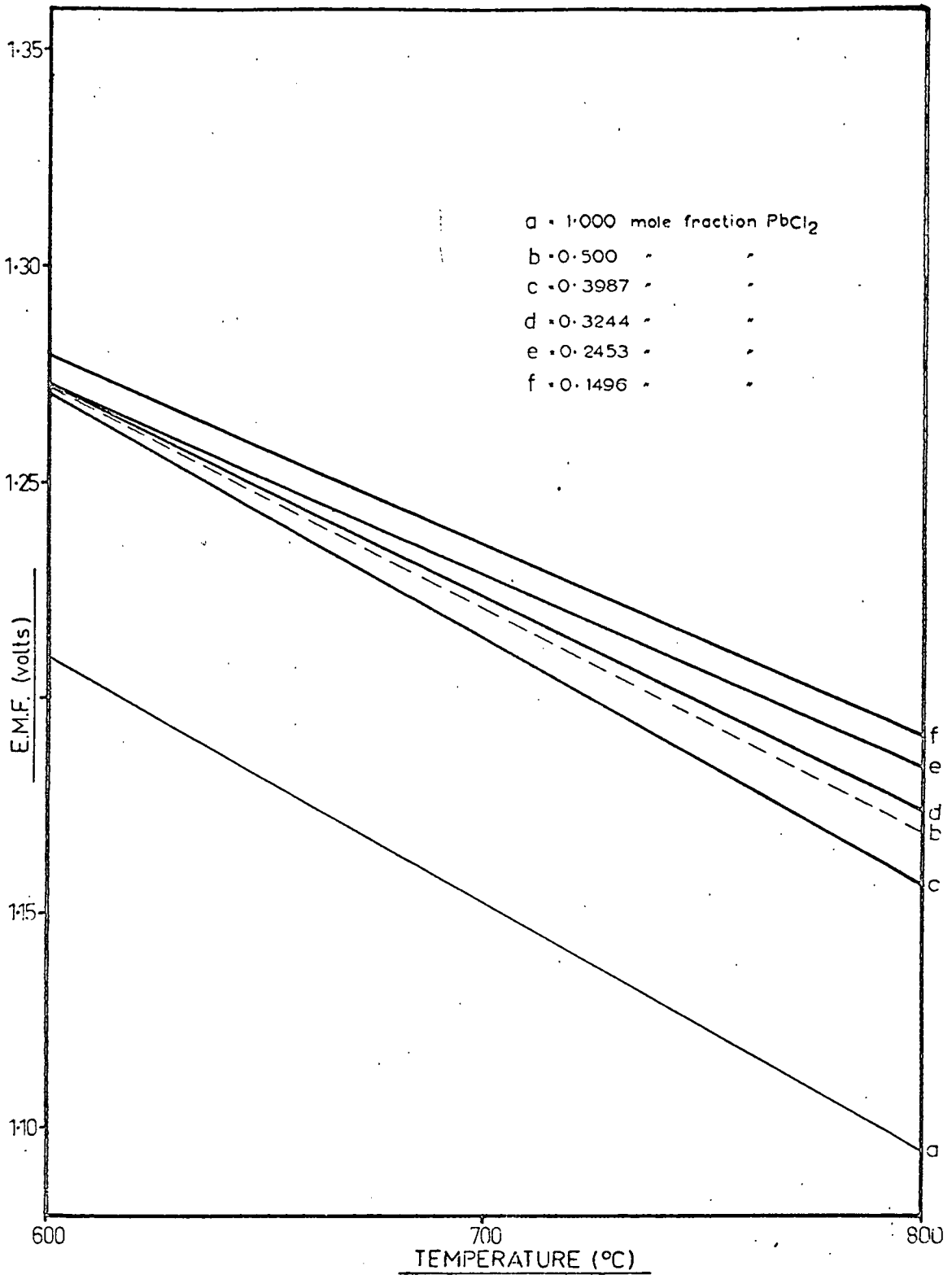



FIG. 3·26

SYSTEM $(xPbCl_2 + xCsCl)—(1-2x)LiCl$

E.M.F. vs TEMPERATURE

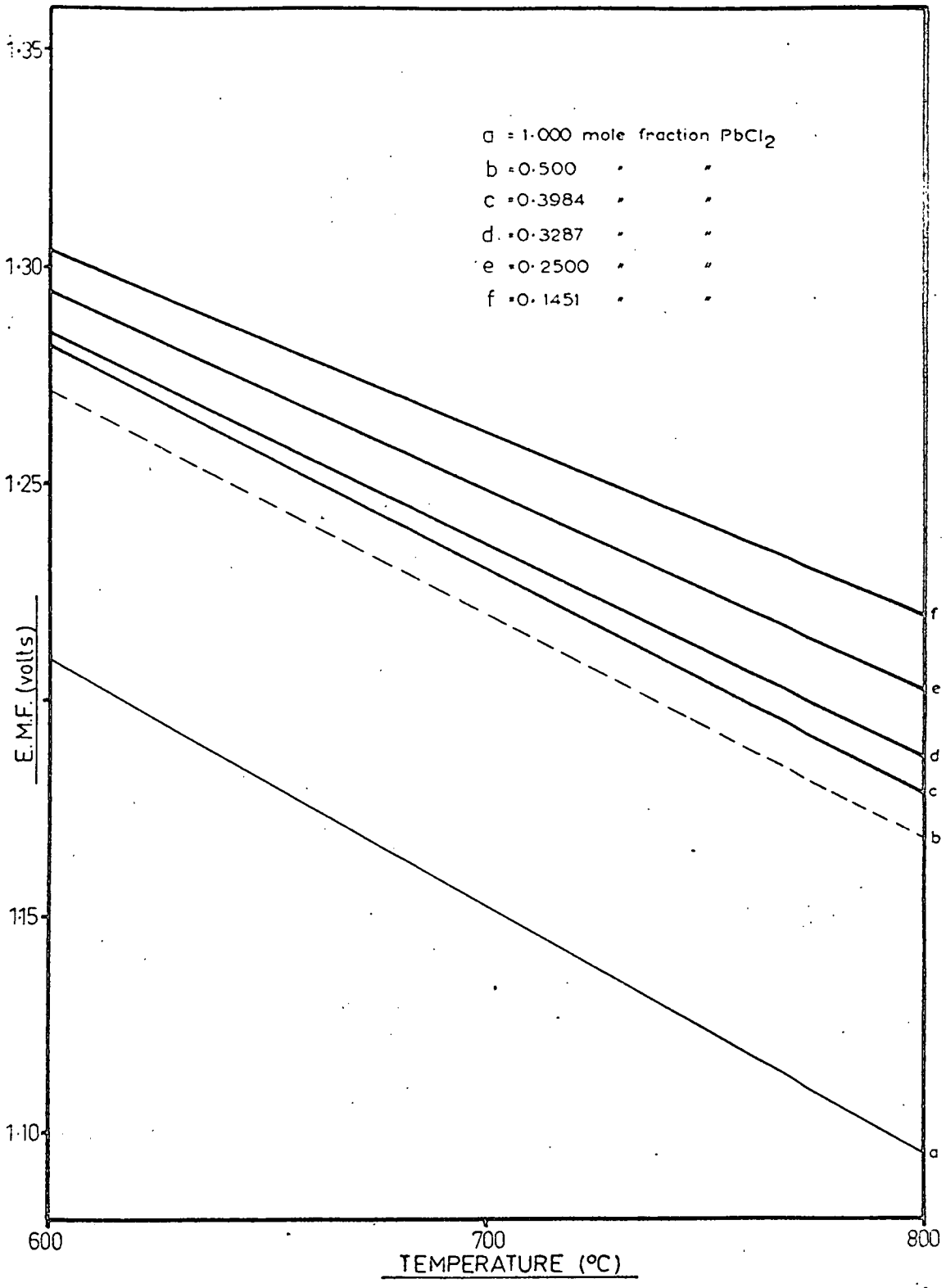



FIG. 3-27

SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)NaCl$

E.M.F. vs TEMPERATURE

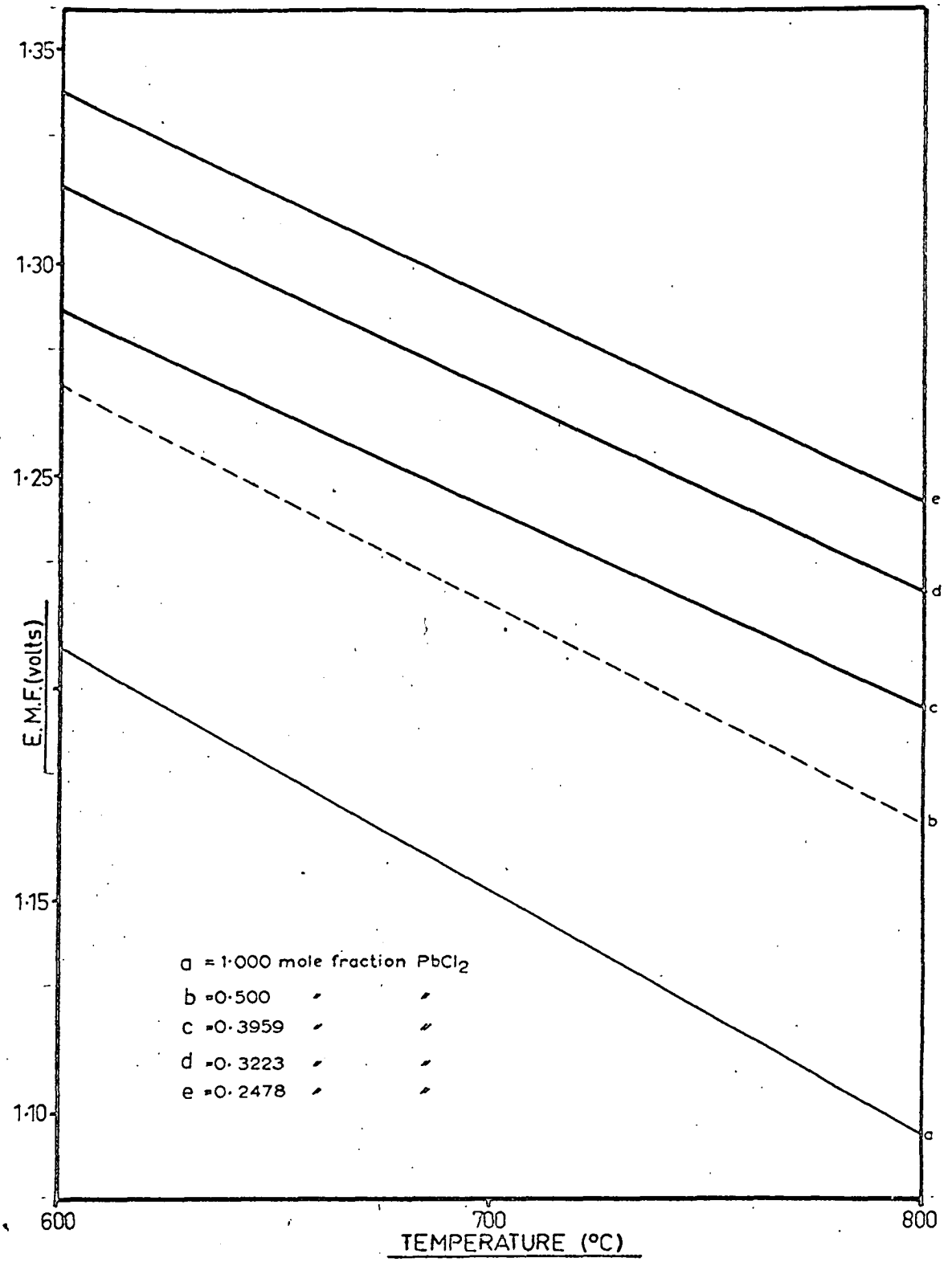



FIG. 3·28

SYSTEM $(x\,PbCl_2 + x\,CsCl) - (1-2x)\,KCl$

E.M.F. vs TEMPERATURE

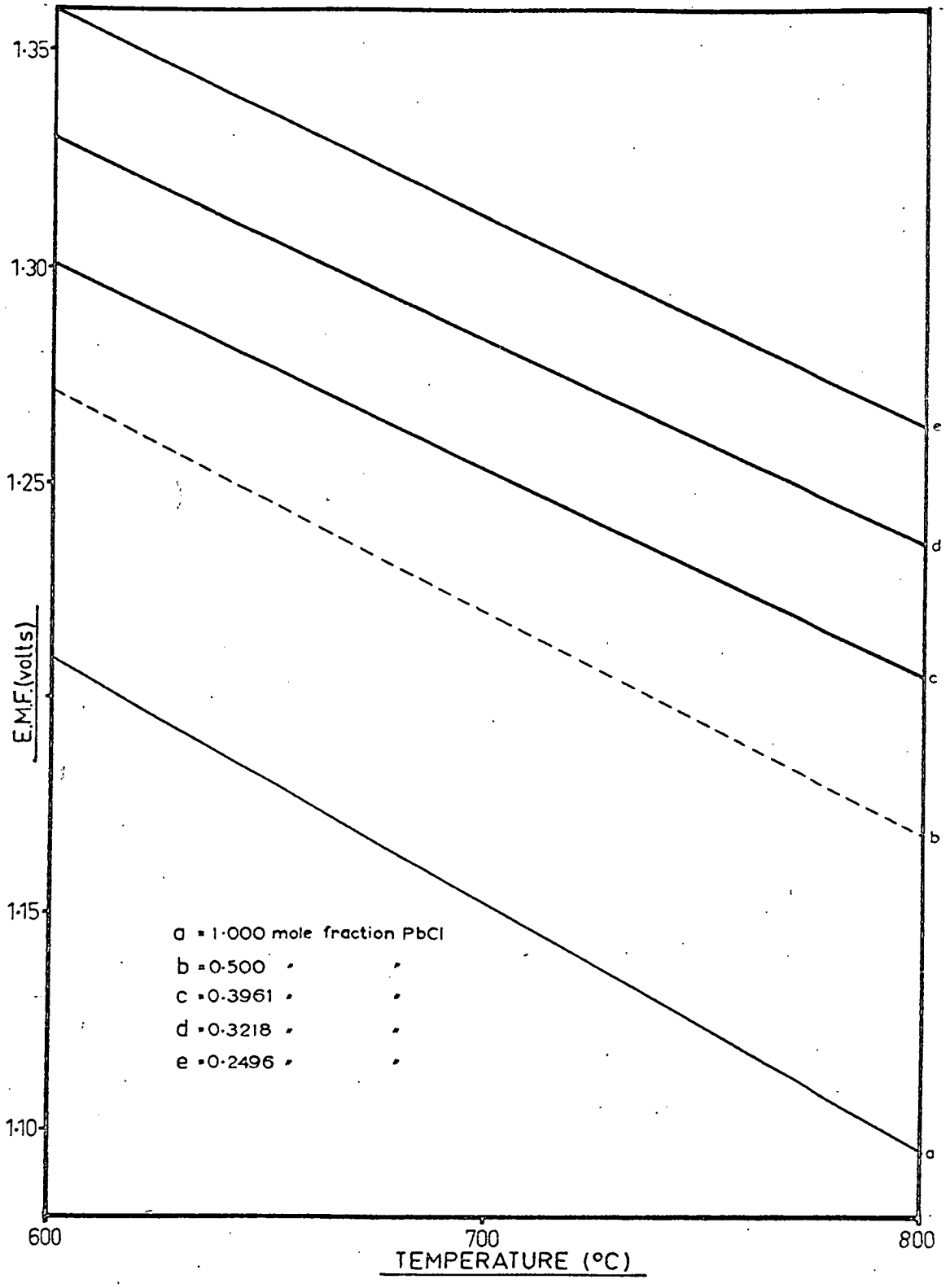



FIG. 3·29

SYSTEM $(x PbCl_2 + x CsCl) - (1-2x) RbCl$

E.M.F. vs. TEMPERATURE

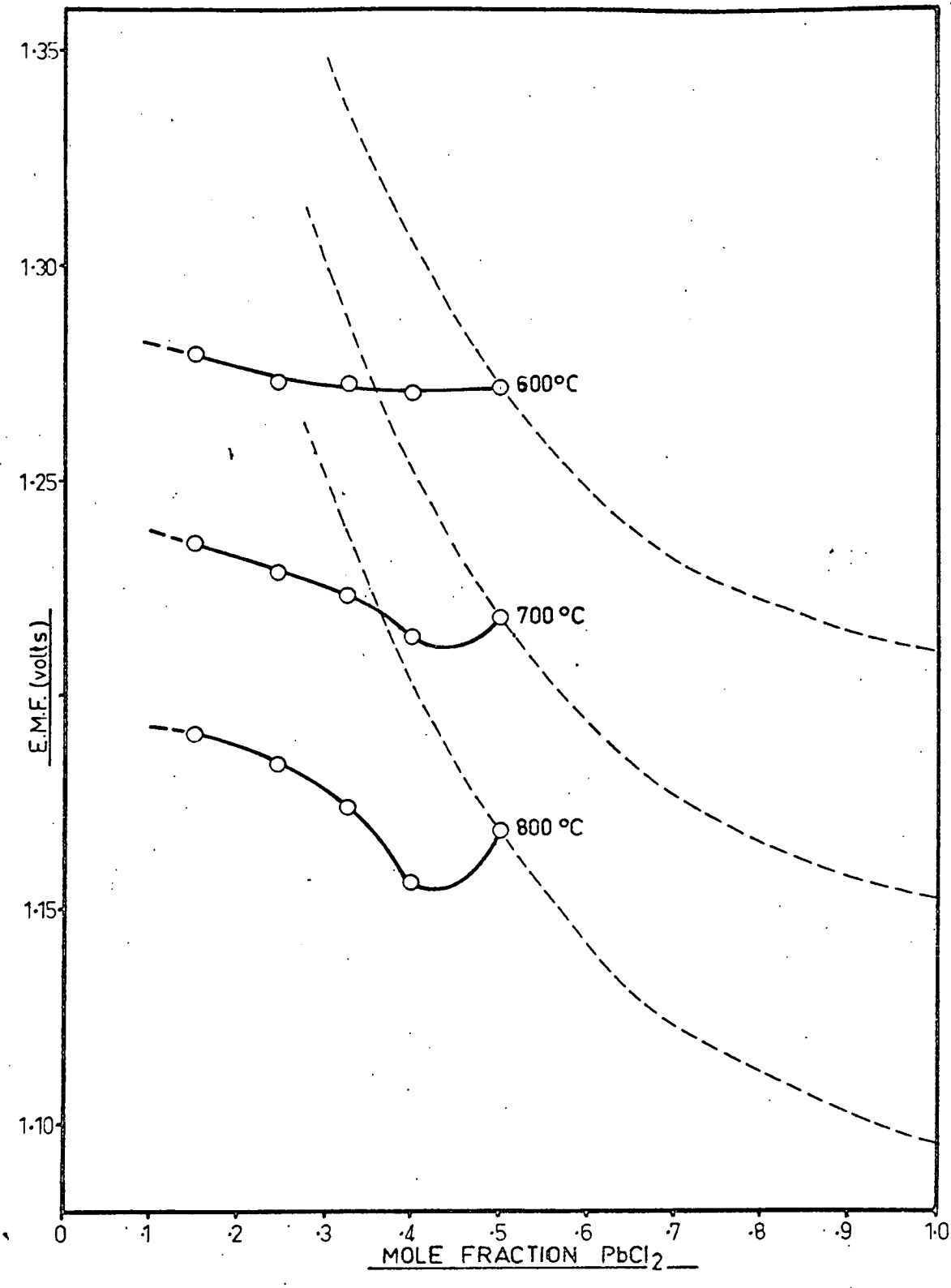



FIG. 3·30

SYSTEM $(xPbCl_2+xCsCl)-(1-2x)LiCl$

E.M.F. vs COMPOSITION

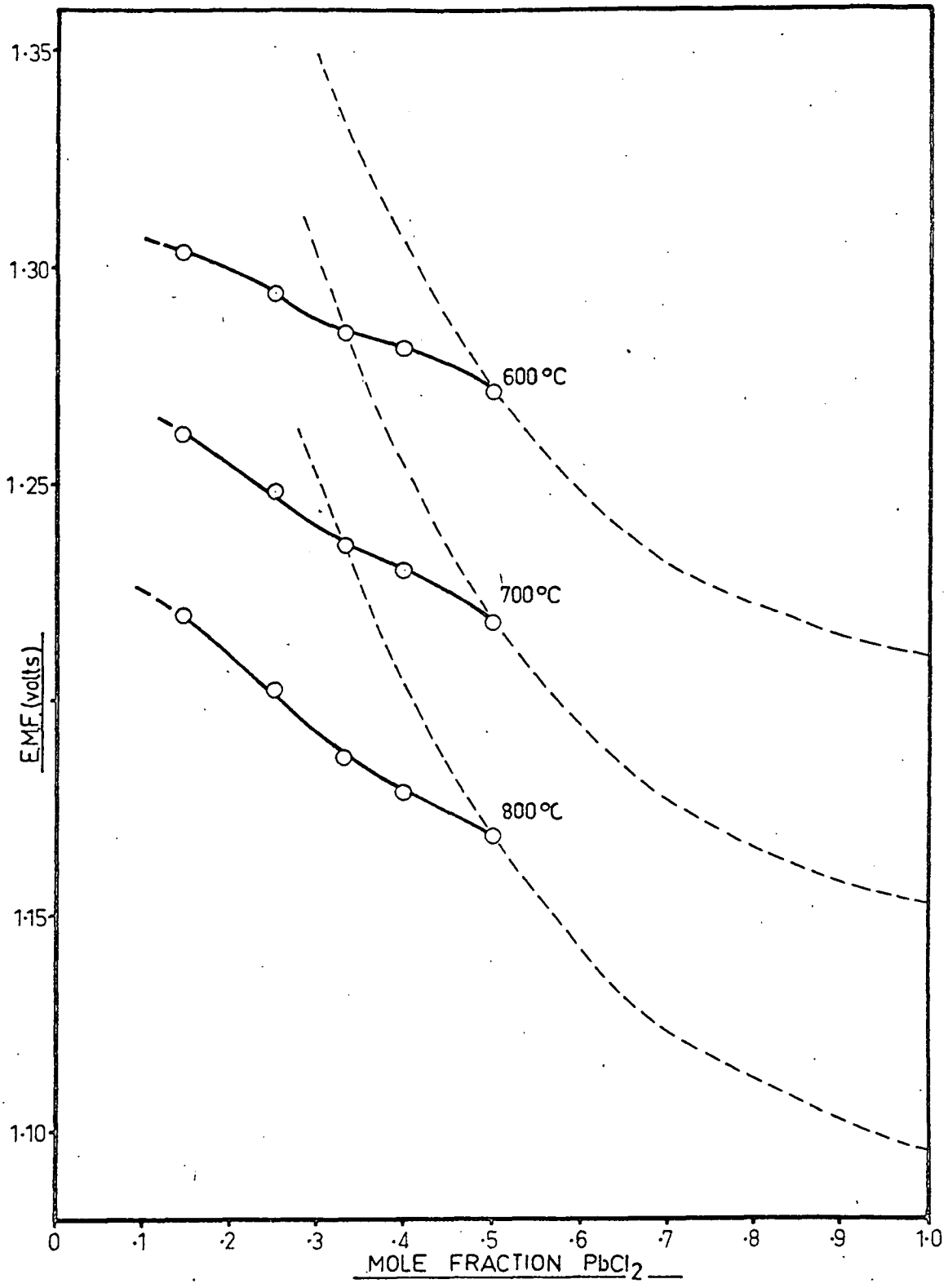



FIG. 3·31 SYSTEM ($xPbCl_2$+$xCsCl$)—(1–2x) NaCl
E.M.F. vs COMPOSITION

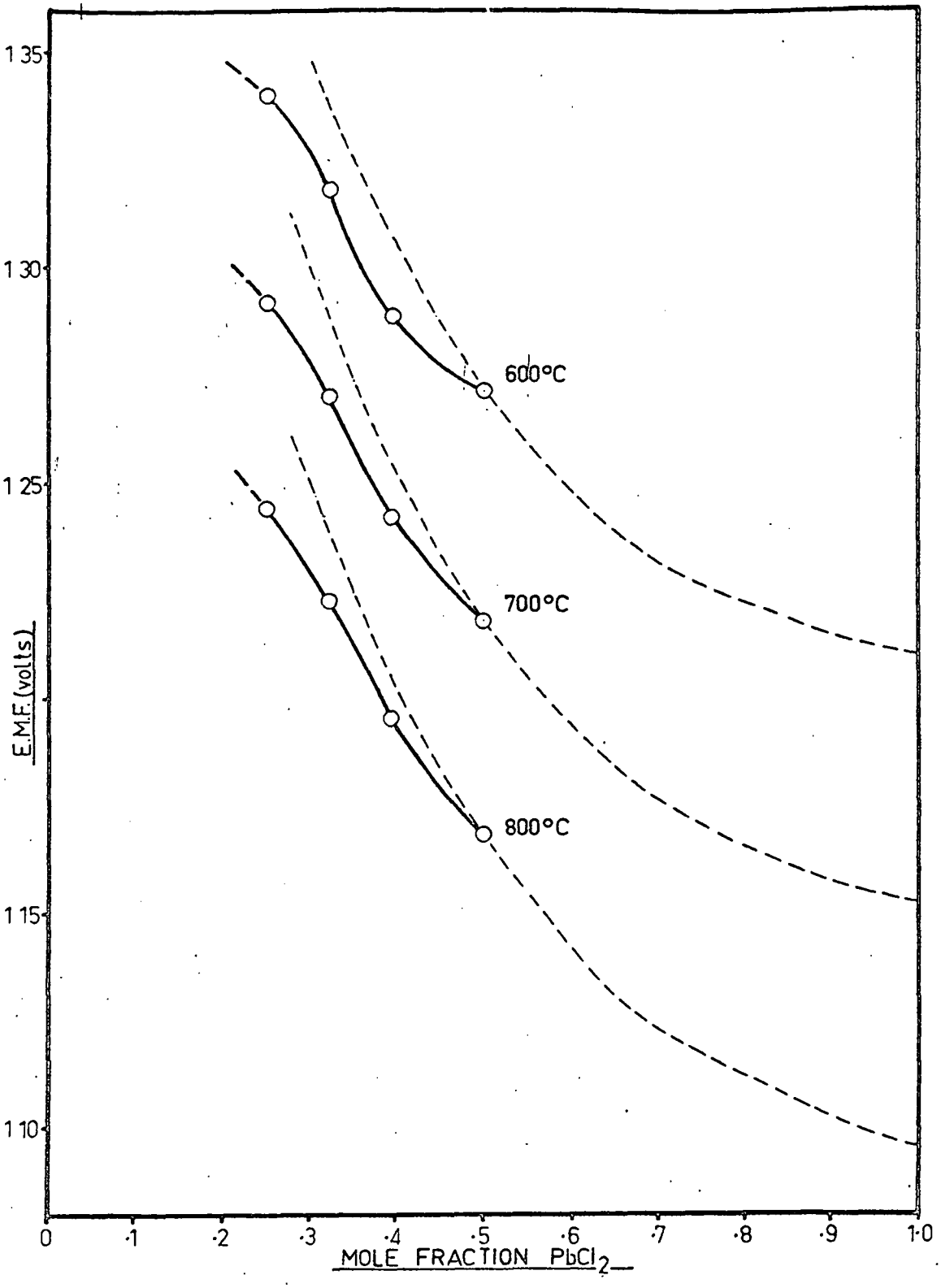



FIG. 3-32 SYSTEM $(xPbCl_2+xCsCl)-(1-2x)KCl$

EMF vs COMPOSITION

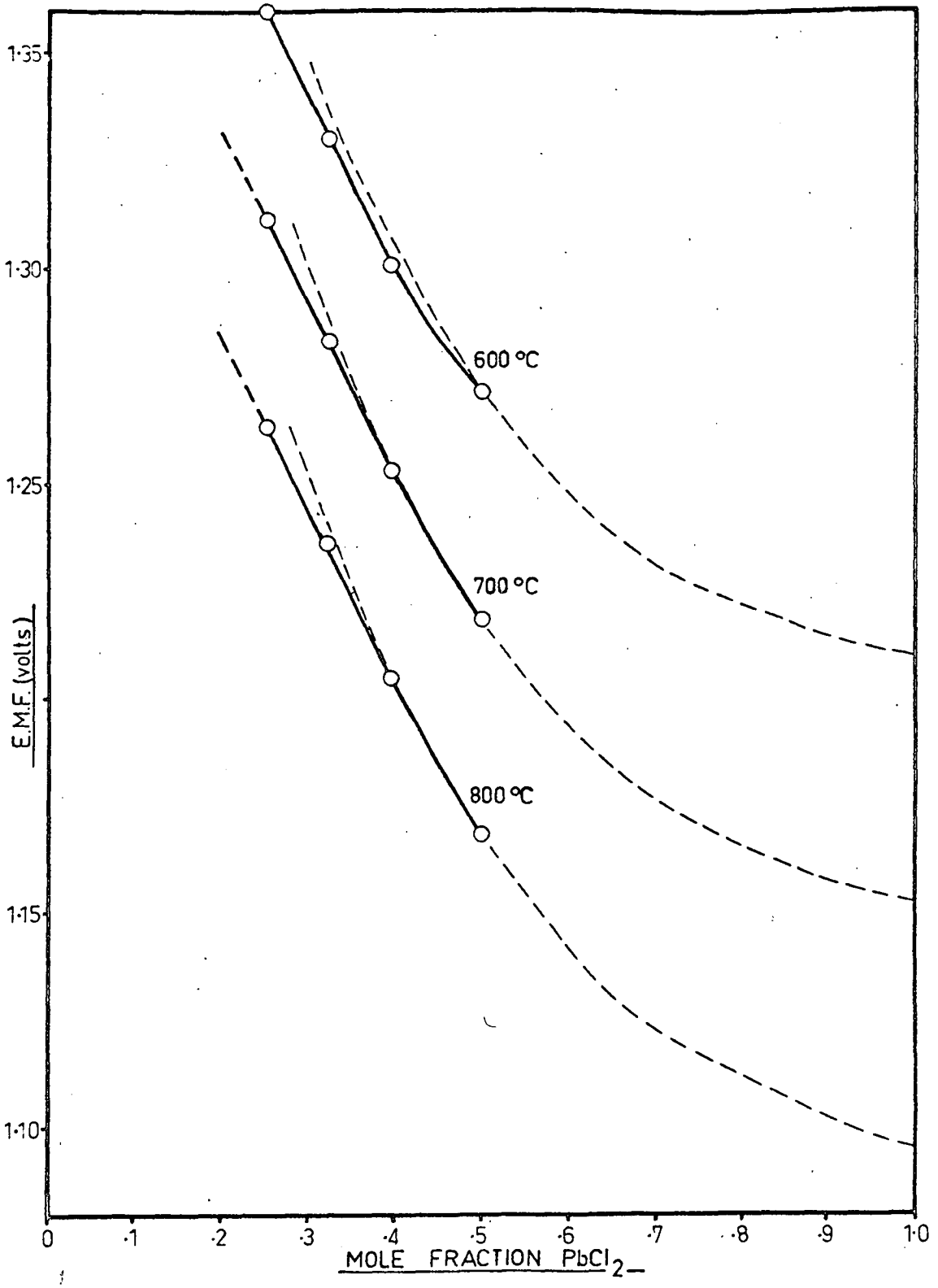
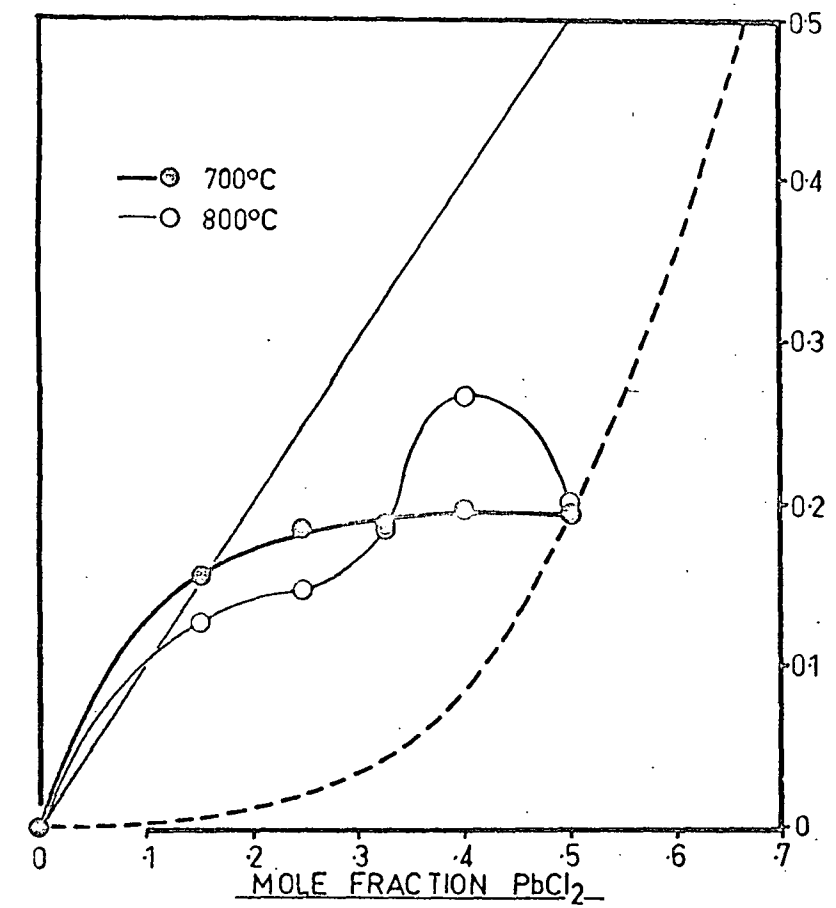



FIG. 3·33 SYSTEM $(xPbCl_2+xCsCl)-(1-2x)RbCl$
E.M.F. vs COMPOSITION




ACTIVITY $PbCl_2$

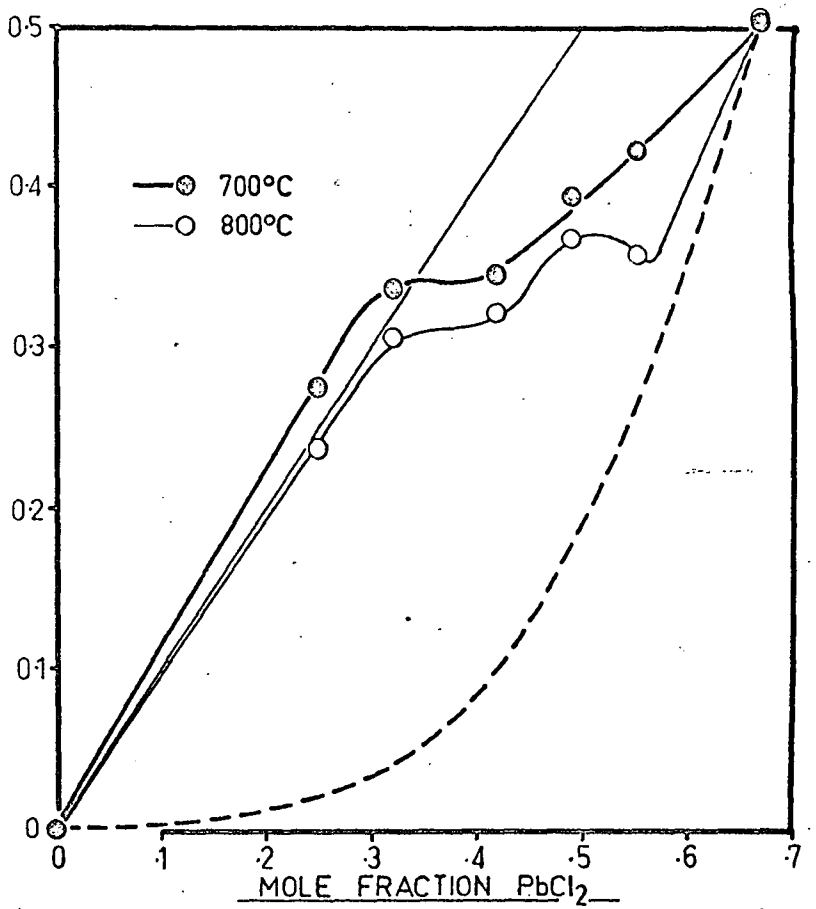



FIG. 3·34 ACTIVITY $PbCl_2$ vs COMPOSITION

(A.) SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)LiCl$

(B.) SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)LiCl$

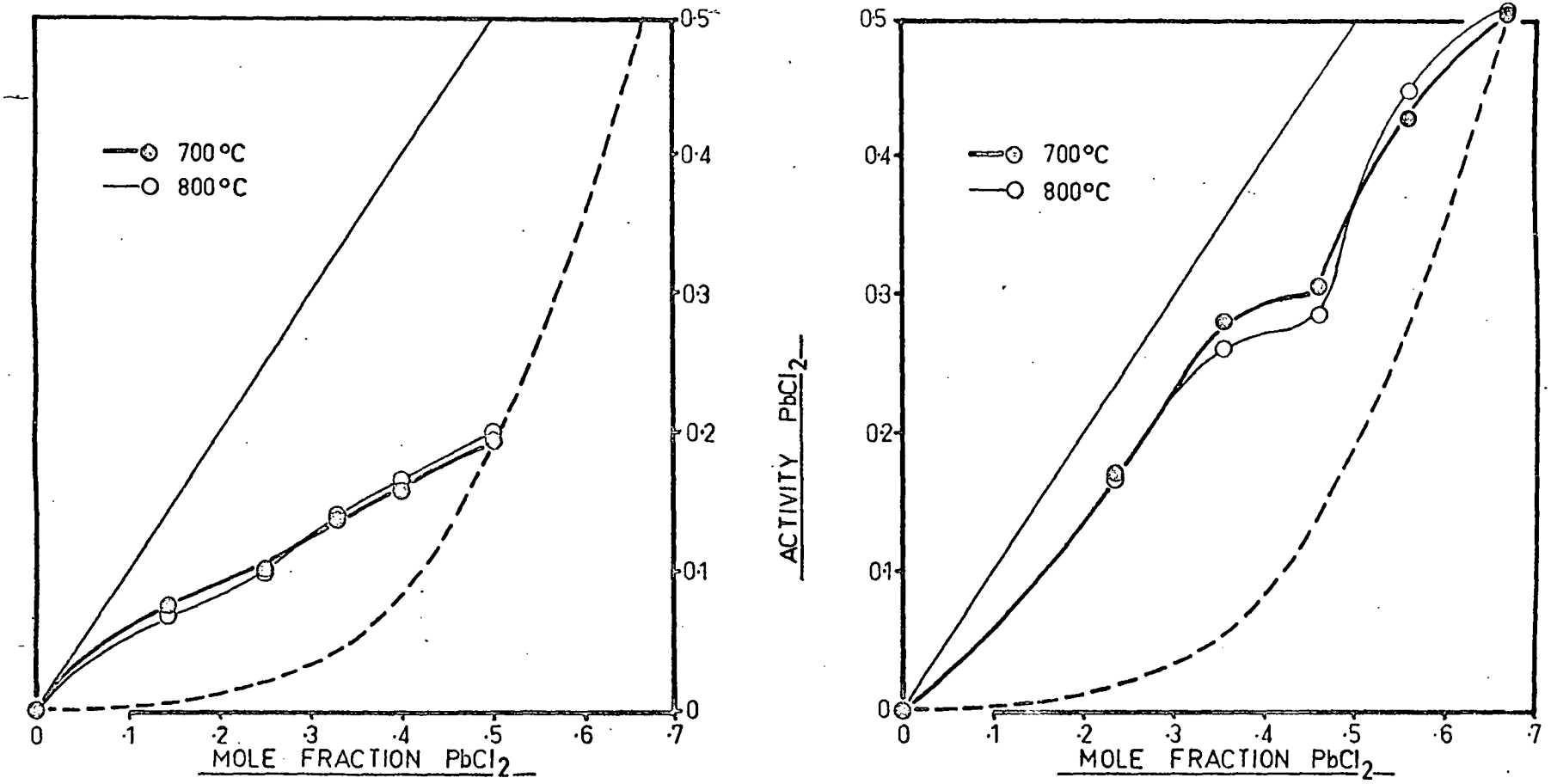



FIG. 3·35 ACTIVITY $PbCl_2$ vs COMPOSITION

(A.) SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)NaCl$

(B.) SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)NaCl$

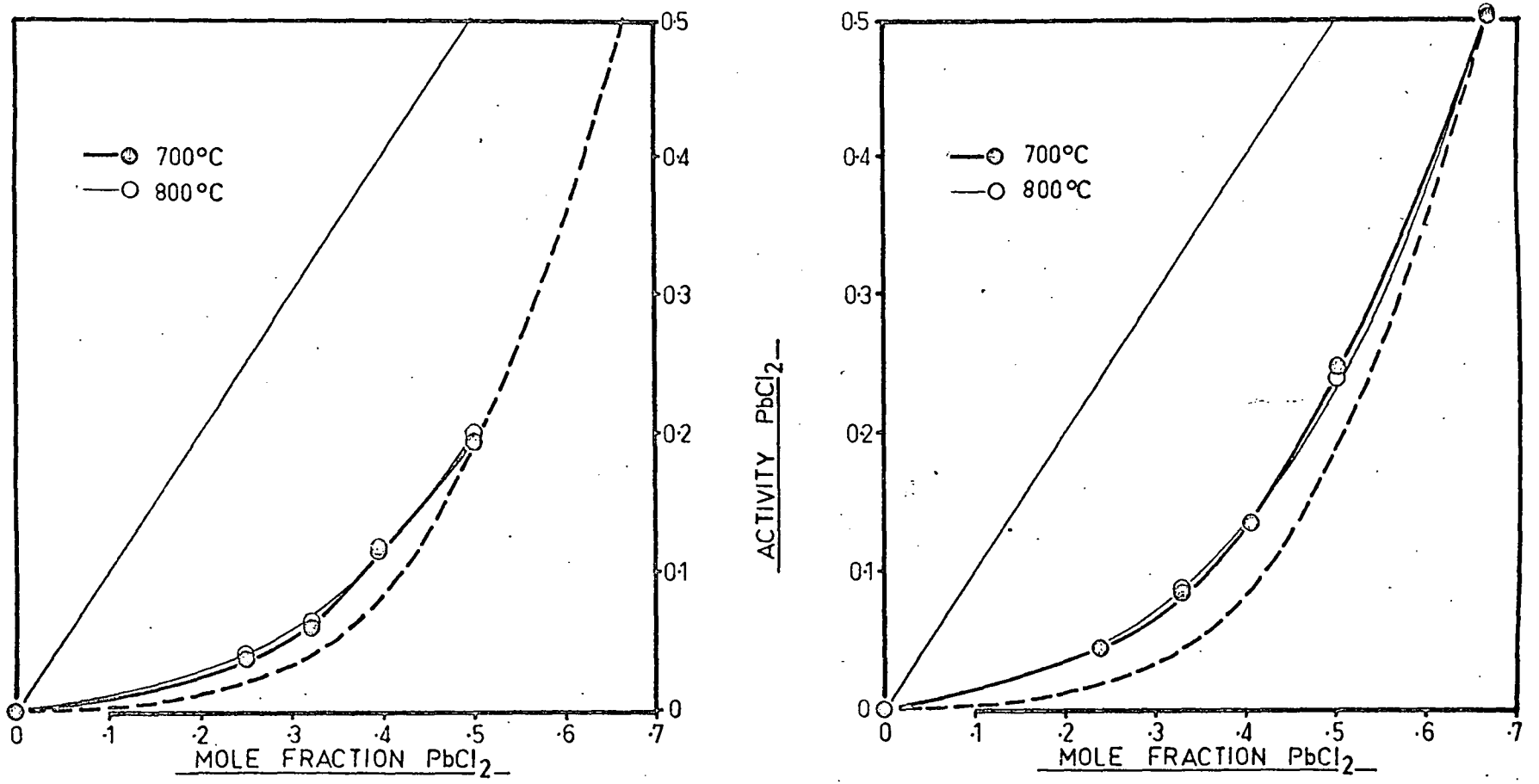



FIG. 3·36 ACTIVITY $PbCl_2$ vs COMPOSITION

(A.) SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)KCl$ (B.) SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)KCl$

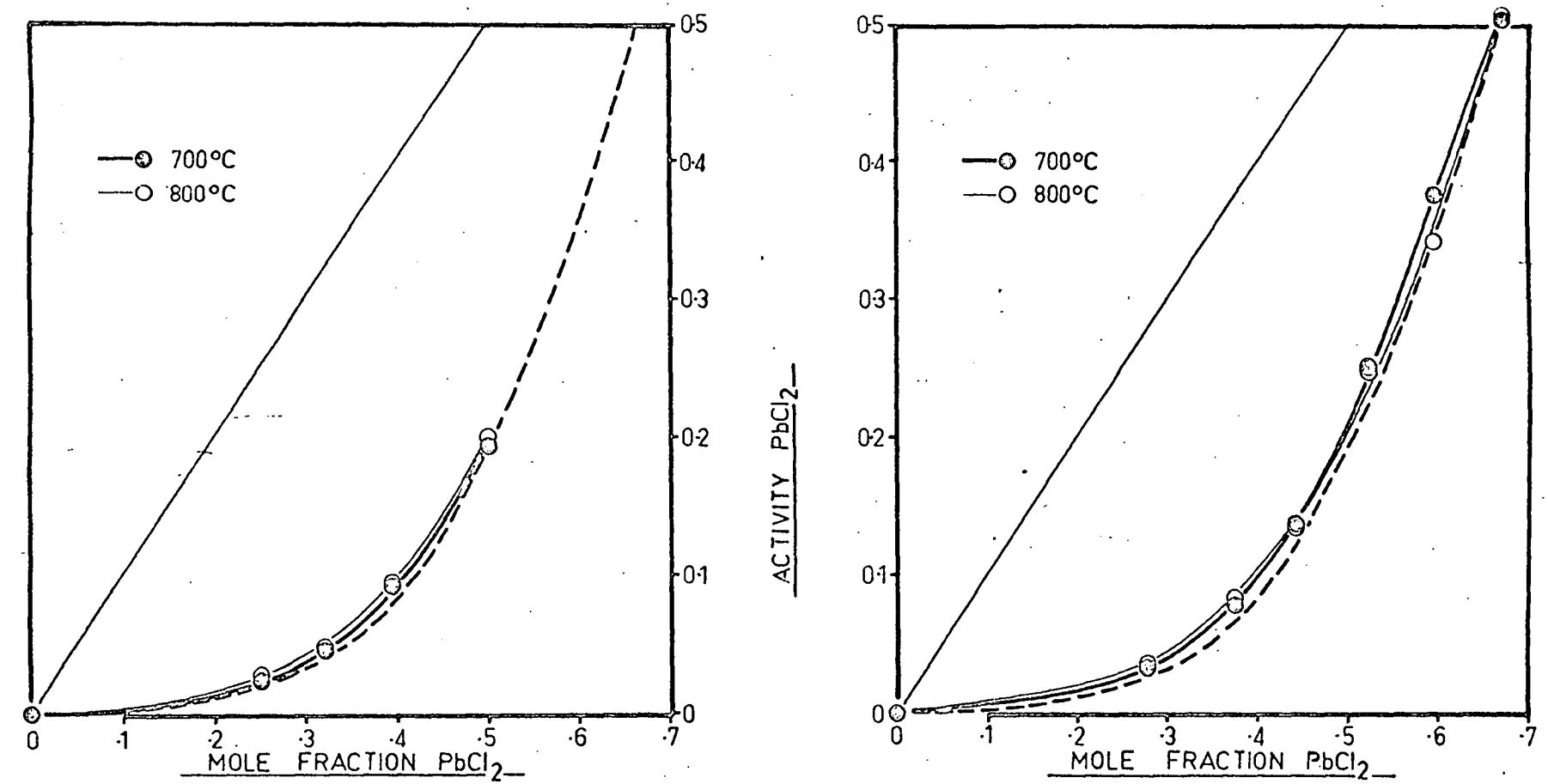



FIG. 3·37 ACTIVITY $PbCl_2$ vs COMPOSITION

(A.) SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)RbCl$ (B.) SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)RbCl$

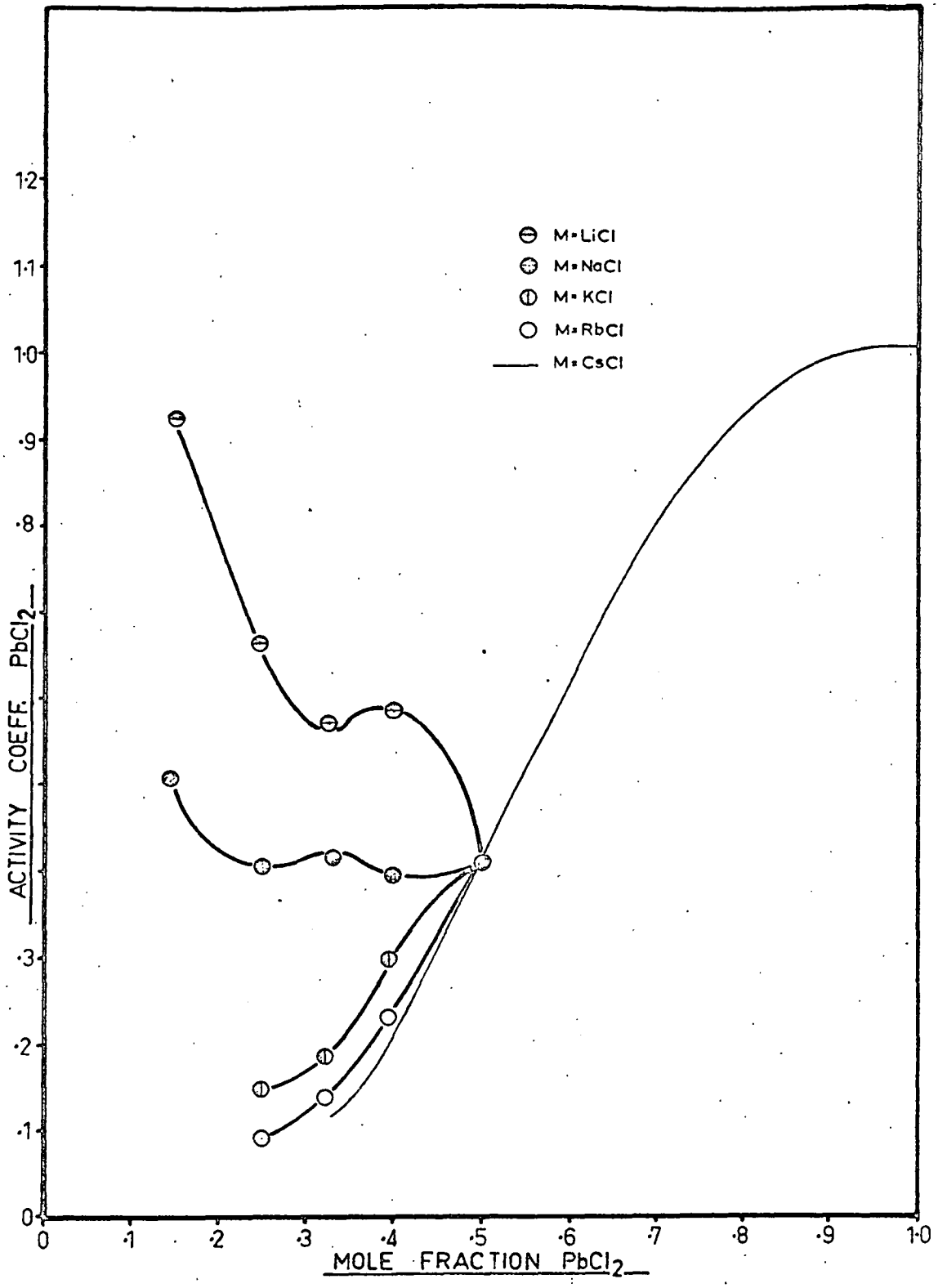
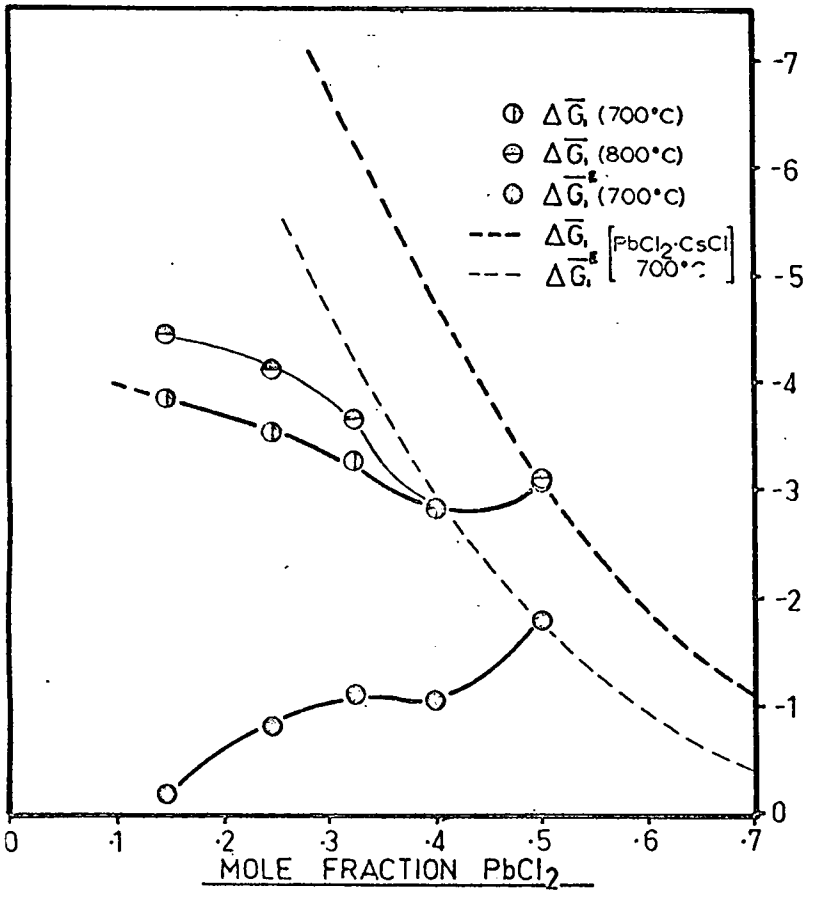



FIG. 3·38 SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)MCl$
ACTIVITY COEFF. $PbCl_2$ (700°C) vs COMPOSITION



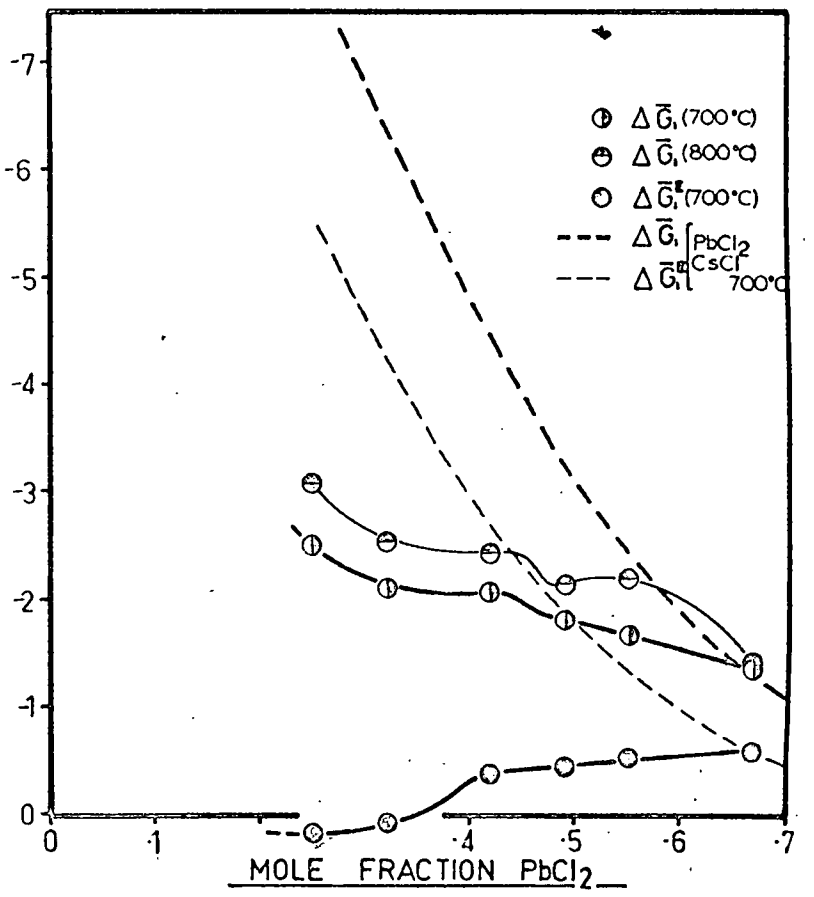
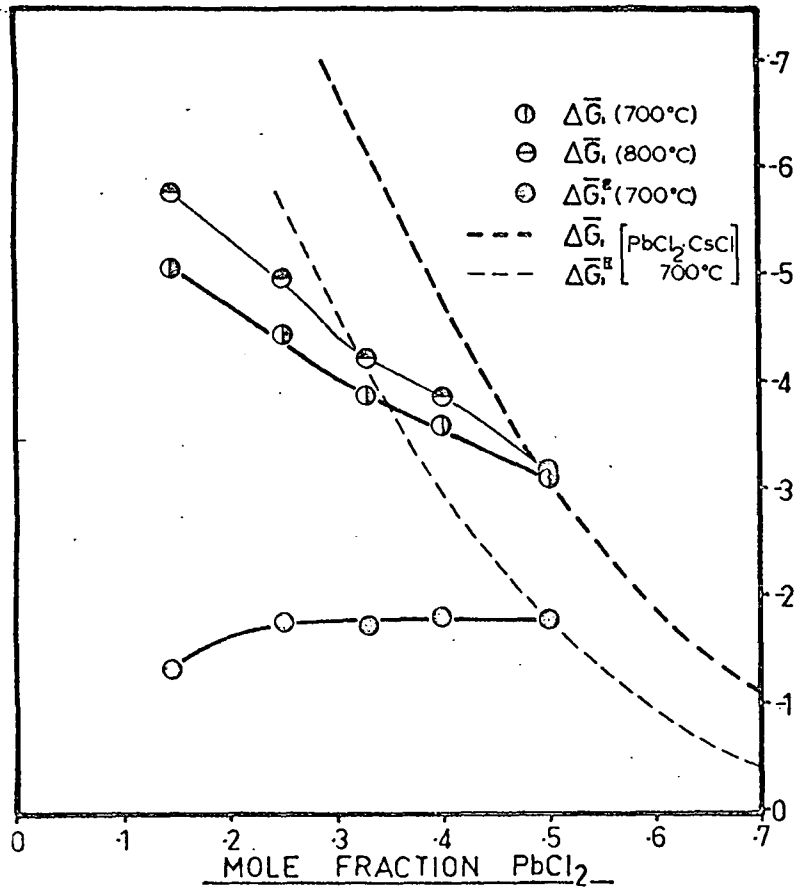




FIG. 3·39 PARTIAL & EXCESS FREE ENERGIES vs COMPOSITION

(A.) SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)LiCl$

(B.) SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)LiCl$



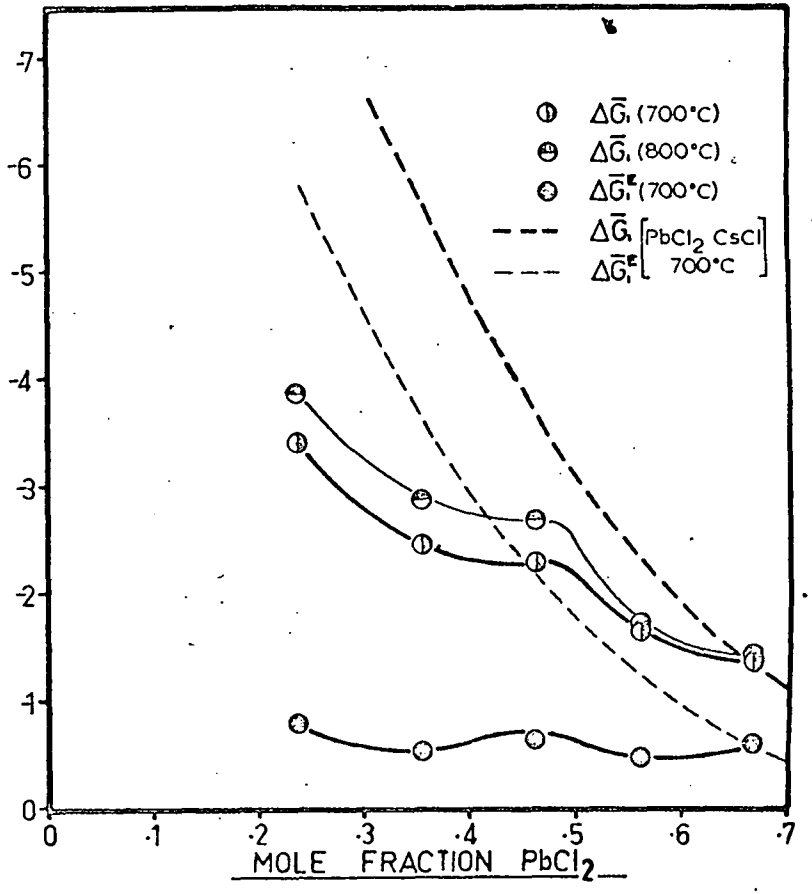




FIG. 3·40 PARTIAL & EXCESS FREE ENERGIES vs COMPOSITION

(A.) SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)NaCl$

(B.) SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)NaCl$

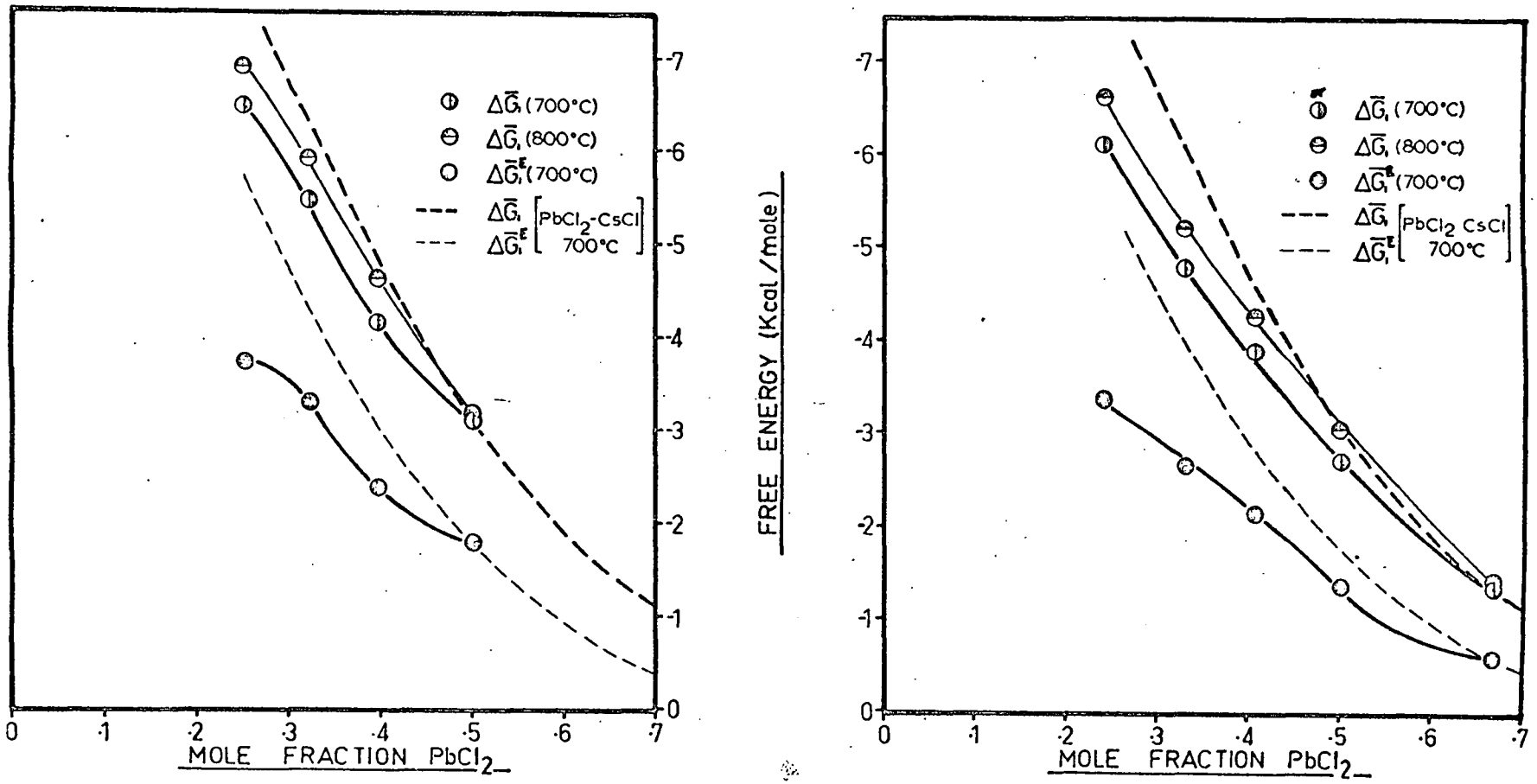



FIG. 3·41 PARTIAL & EXCESS FREE ENERGIES vs COMPOSITION

(A.) SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)KCl$ (B.) SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)KCl$

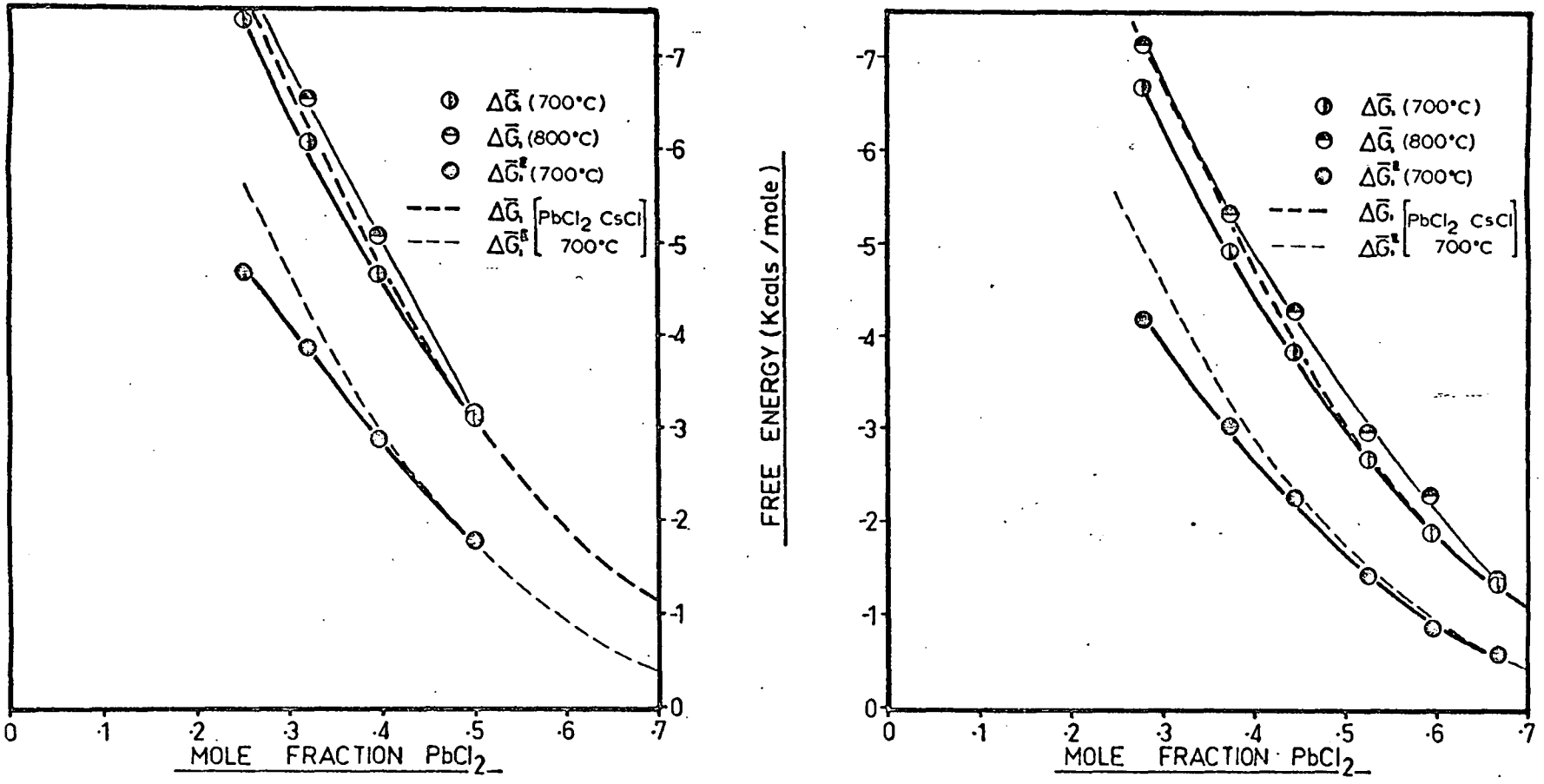



FIG. 3·42 PARTIAL & EXCESS FREE ENERGIES vs COMPOSITION

(A.) SYSTEM $(xPbCl_2 + xCsCl) - (1-2x)\,RbCl$

(B.) SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)\,RbCl$

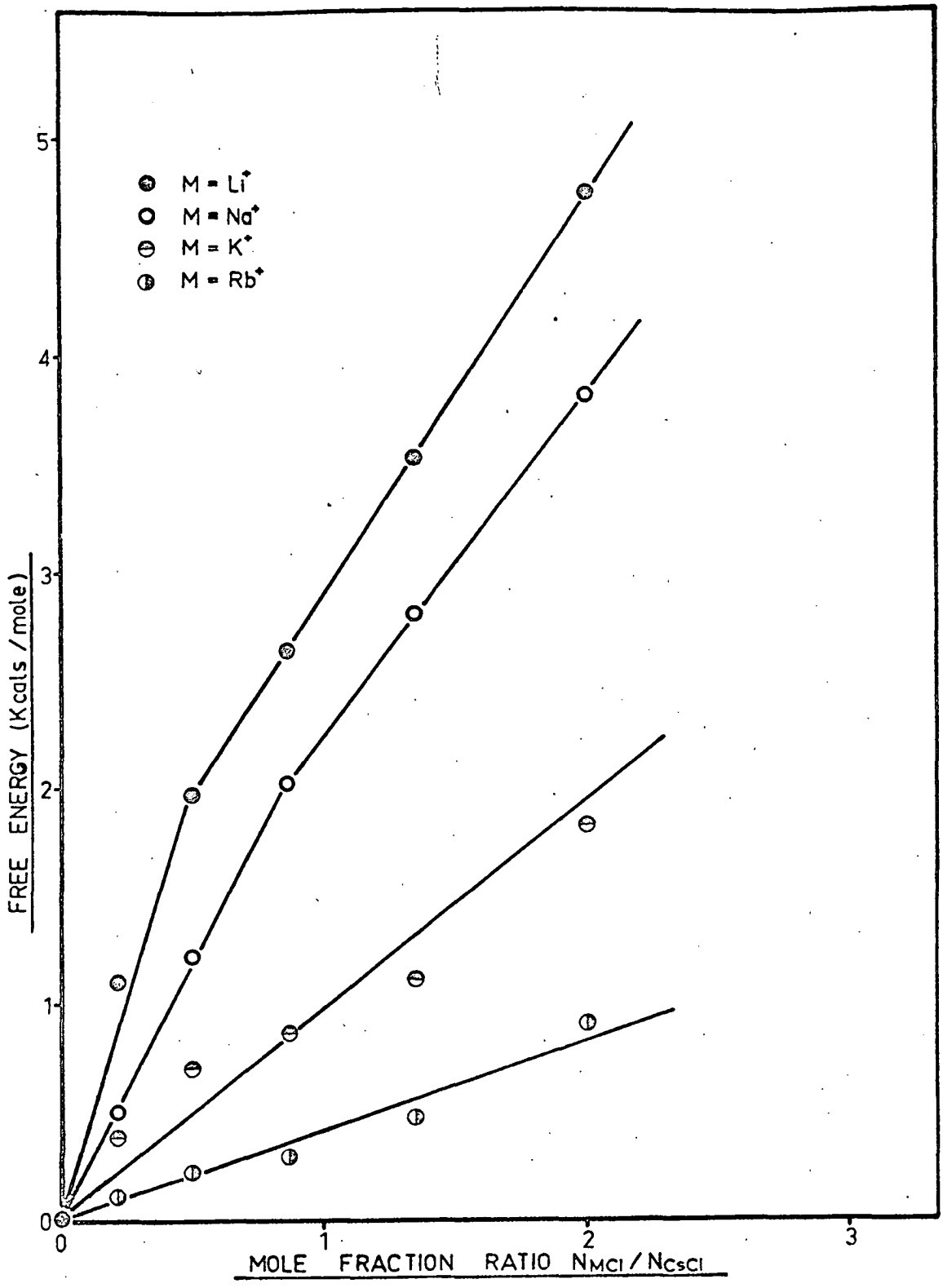



FIG. 3·43 $\left[\Delta\bar{G}_{PbCl_2}\text{ (SYSTEM } PbCl_2\text{–}CsCl\text{ )}\right]$ — $\left[\Delta\bar{G}_{PbCl_2}\text{ (SYSTEM } (xPbCl_2 + xCsCl) - (1-2x)MCl)\right]$ (700°C)

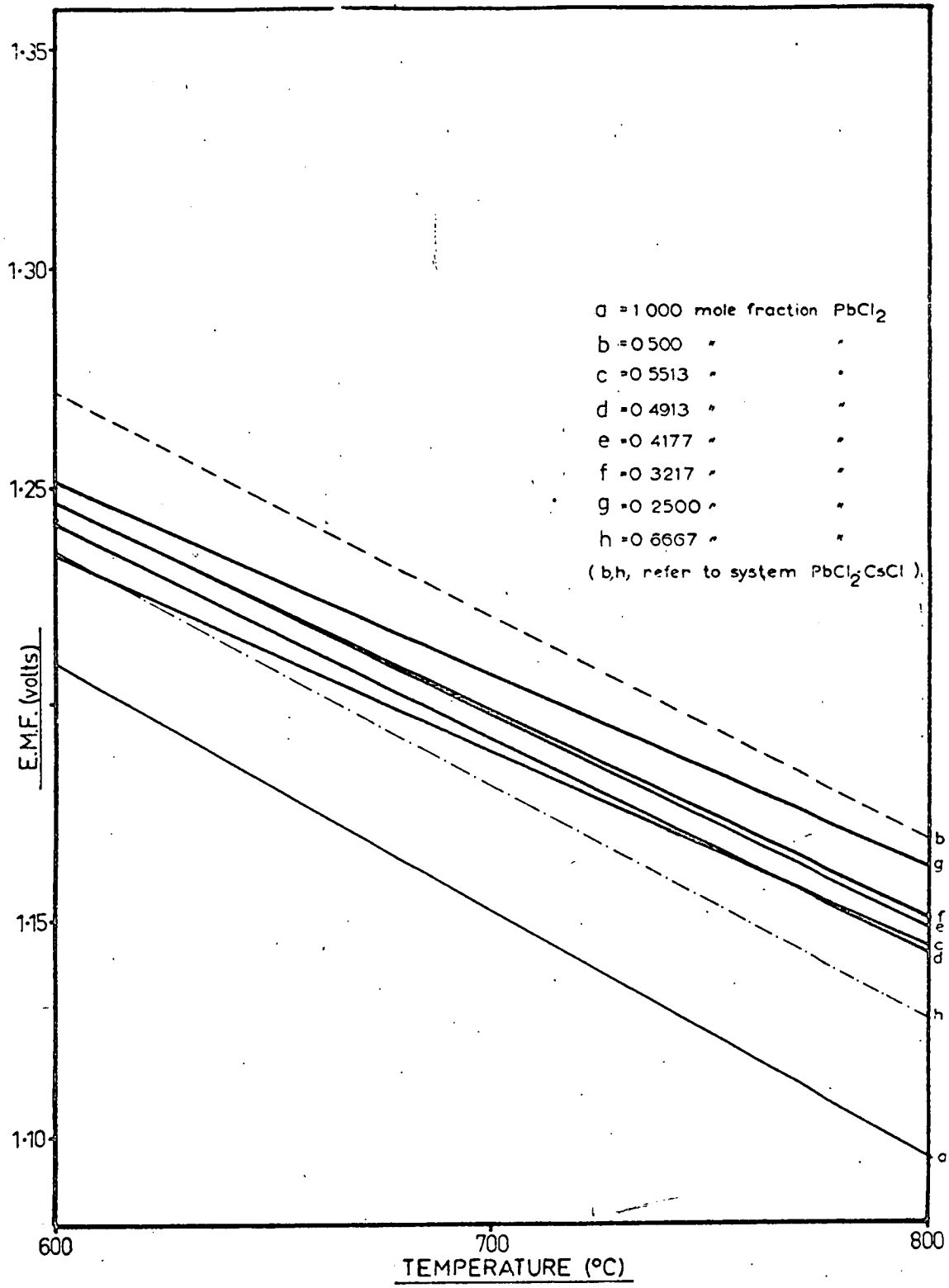



FIG. 3·44

SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)LiCl$

E.M.F. vs. TEMPERATURE

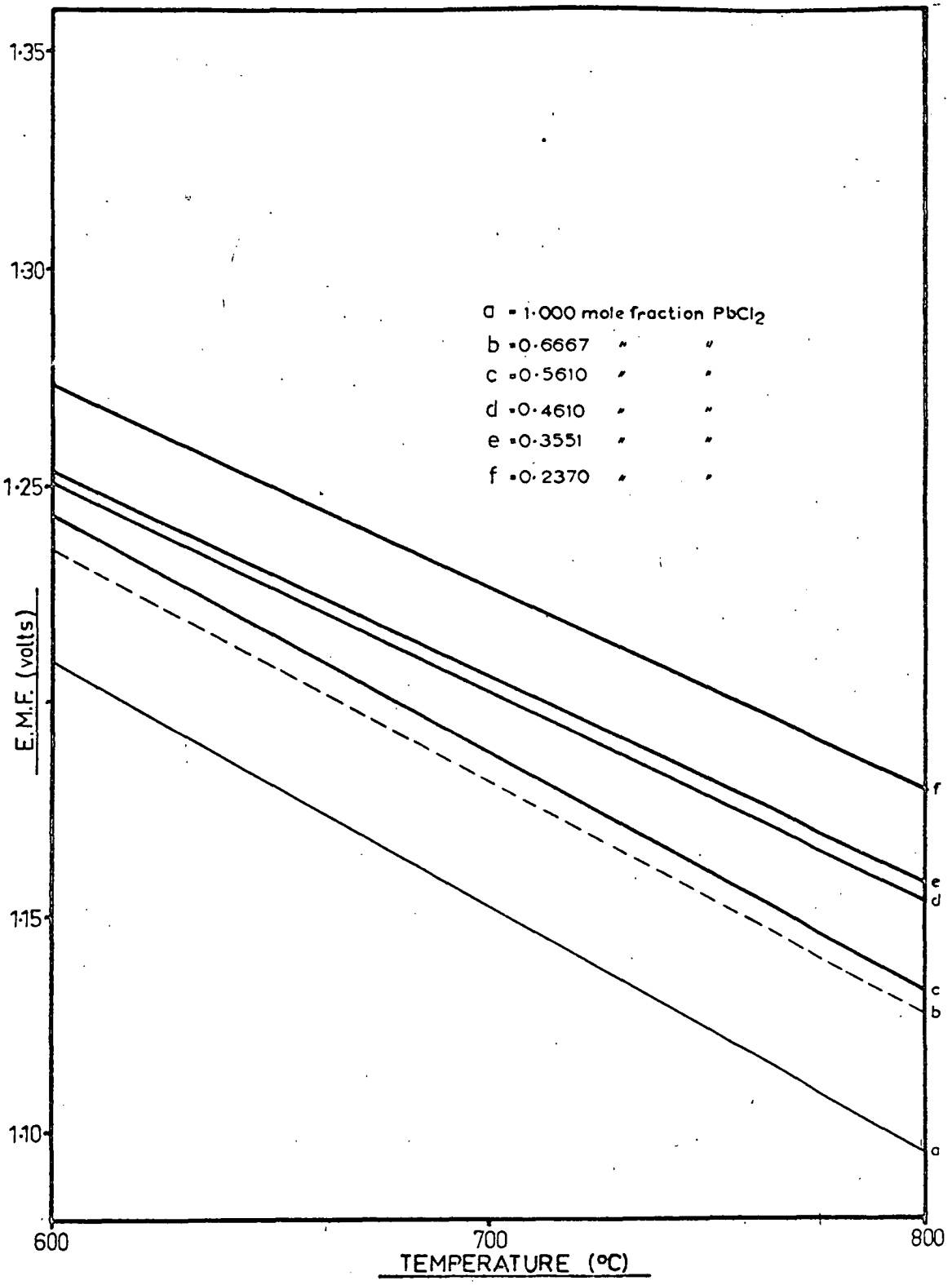



FIG. 3·45

SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)NaCl$

E.M.F. vs TEMPERATURE

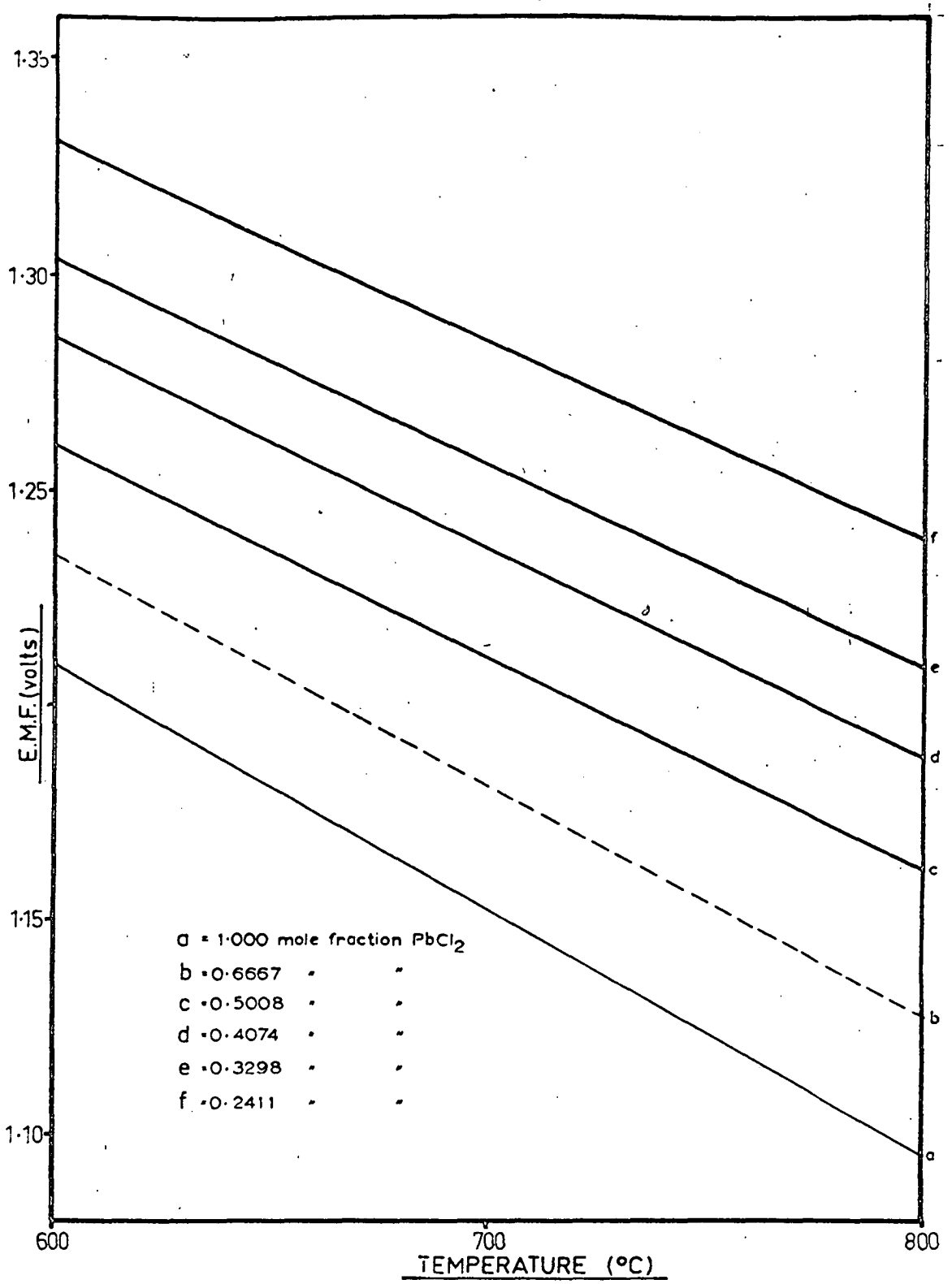



FIG. 3·46

SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)KCl$

E.M.F. vs TEMPERATURE

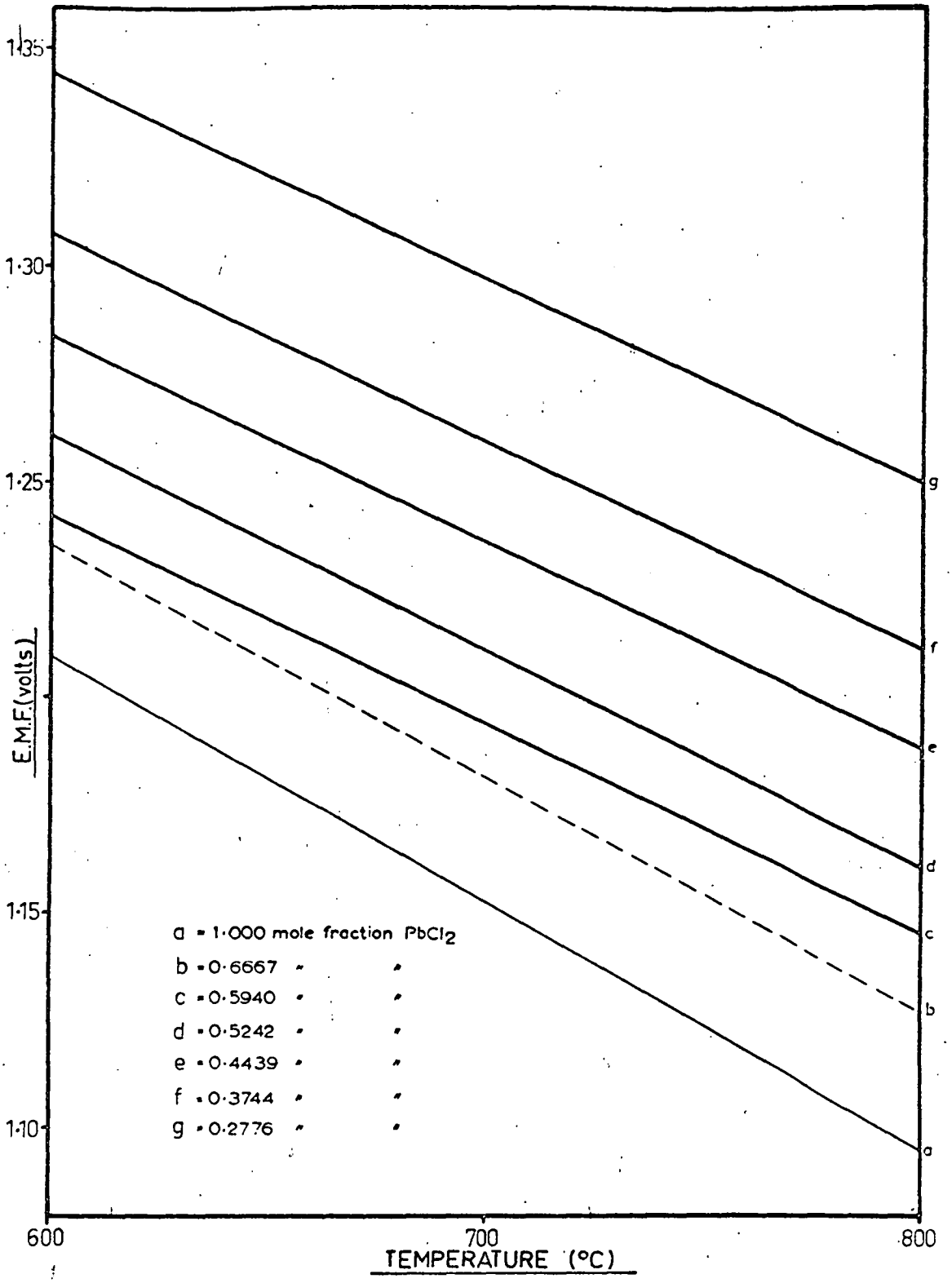



FIG. 3·47

SYSTEM $(2x PbCl_2\ xCsCl)\ (1\ 3x)RbCl$

E.M.F. vs TEMPERATURE

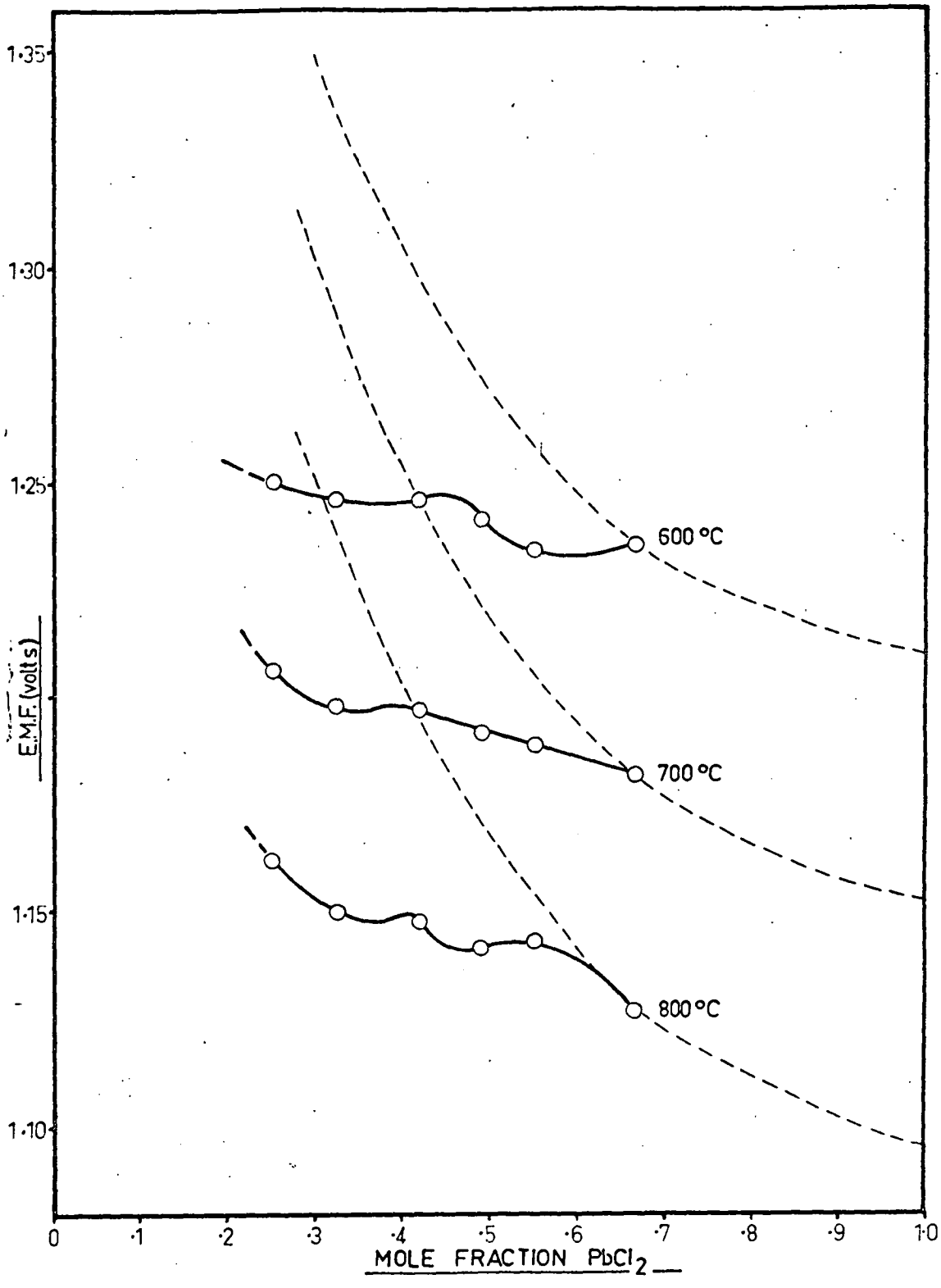



FIG. 3·48

SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)LiCl$
E.M.F. vs COMPOSITION

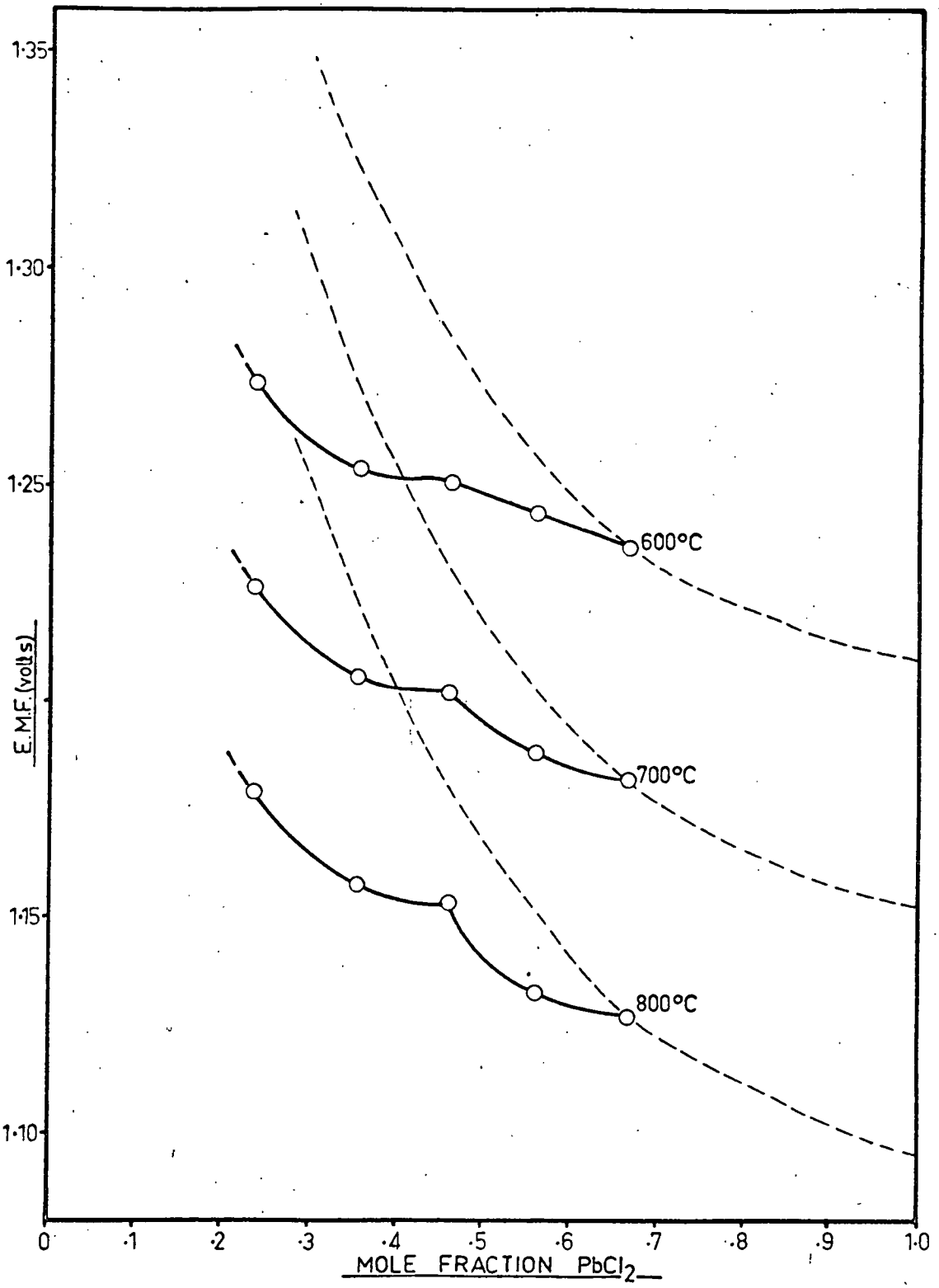



FIG. 3·49

SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)NaCl$

E.M.F. vs COMPOSITION

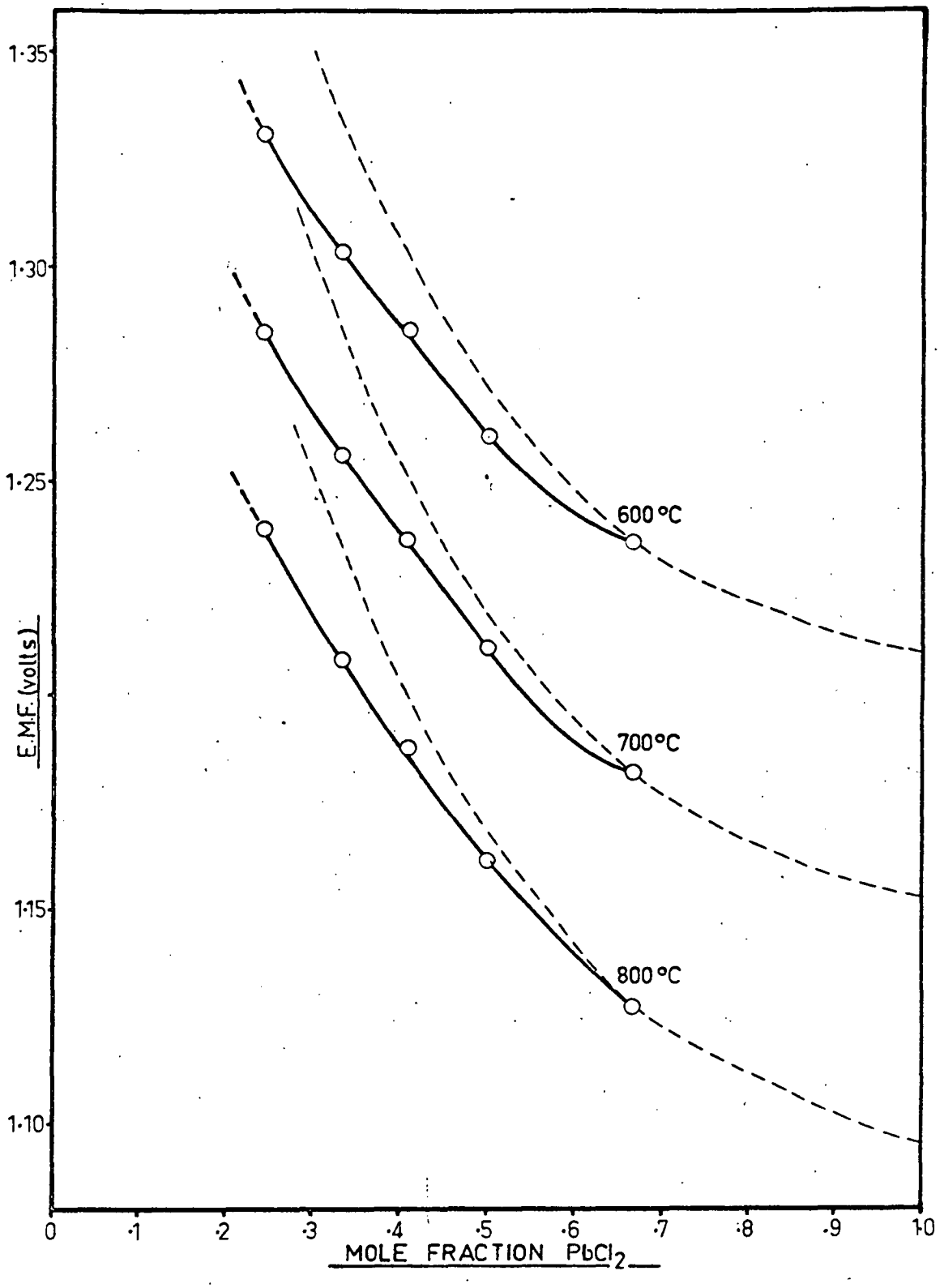



FIG. 3·50 SYSTEM $(2xPbCl_2+xCsCl)-(1-3x)KCl$
E.M.F. vs COMPOSITION

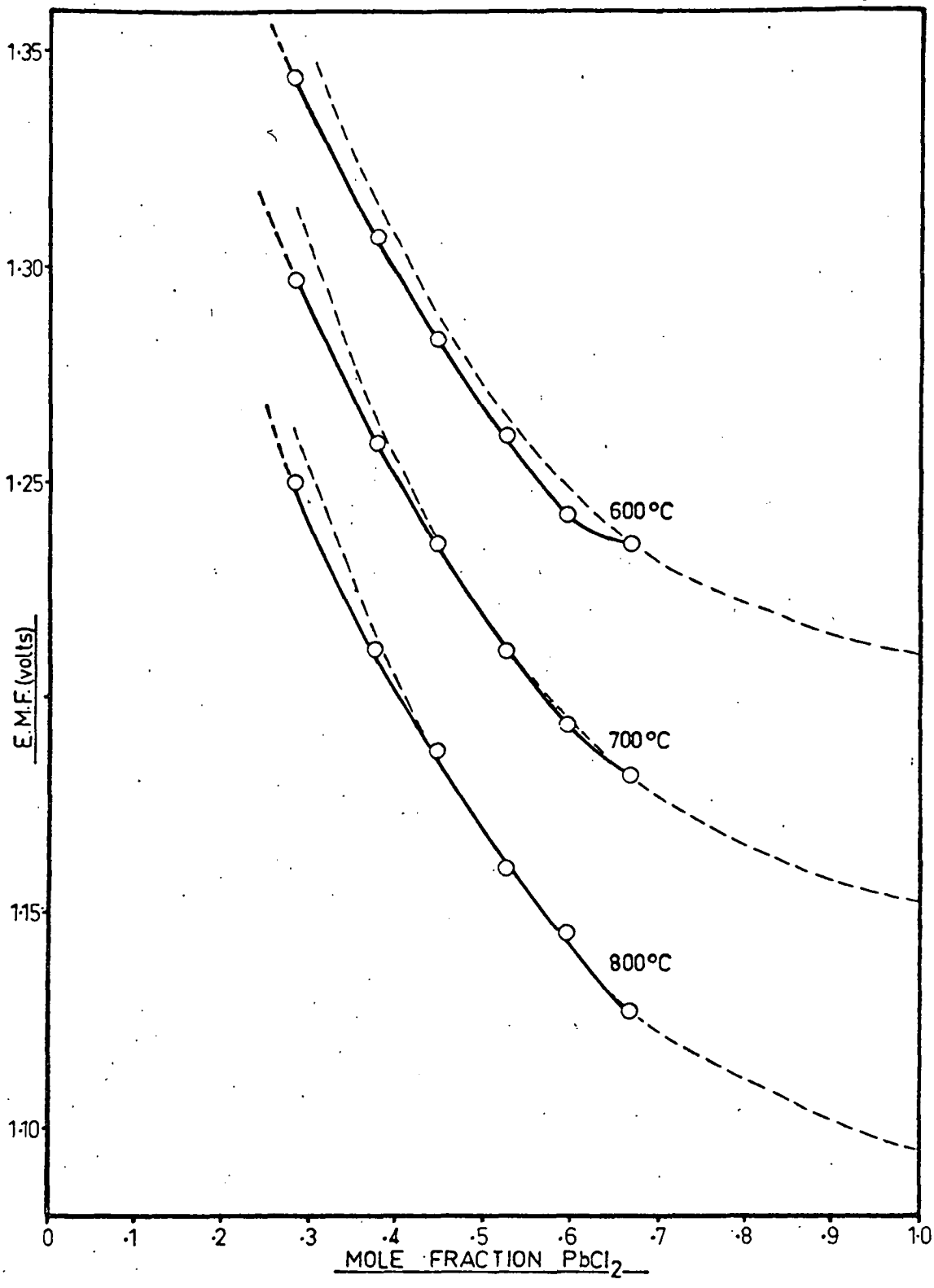



FIG. 3·51 SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)RbCl$

E.M.F. vs COMPOSITION

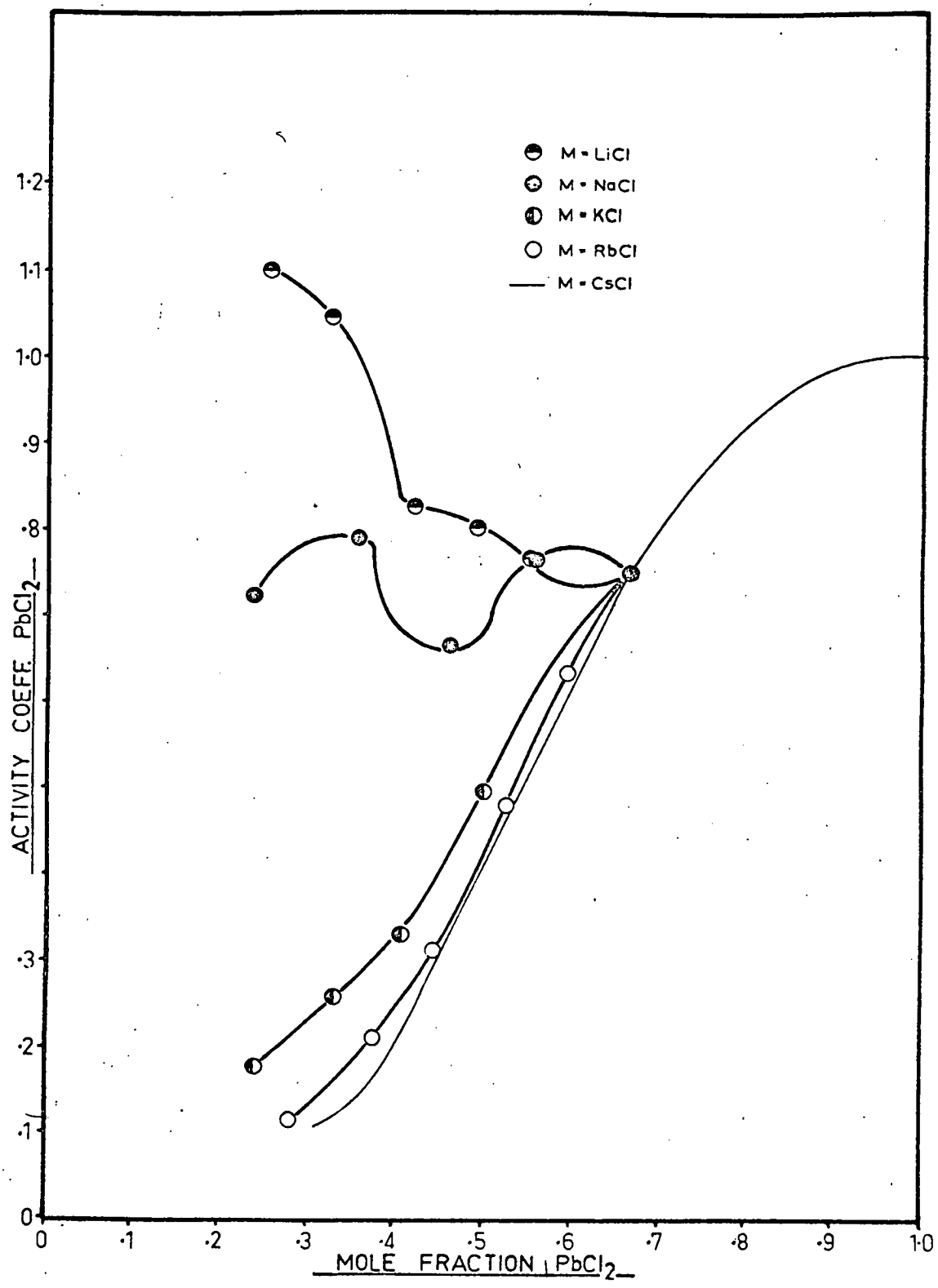



FIG. 3·52 SYSTEM $(2xPbCl_2 + xCsCl) - (1-3x)MCl$

COEFF. ACTIVITY $PbCl_2$ (700°C) vs COMPOSITION

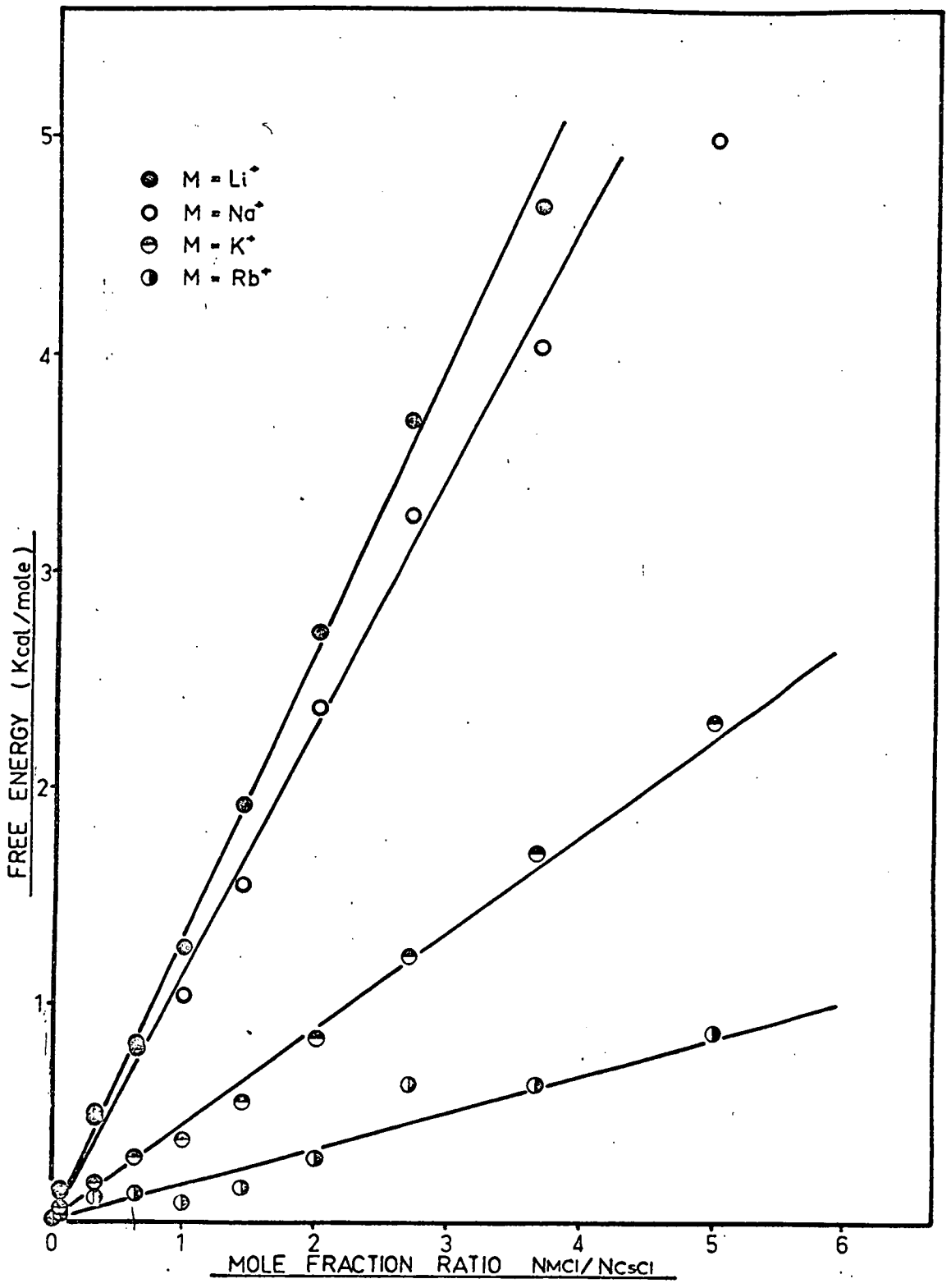



FIG. 3·53 $\frac{[\Delta\bar{G}_{PbCl_2}(\text{SYSTEM } PbCl_2 - CsCl)] -}{[\Delta\bar{G}_{PbCl_2}(\text{SYSTEM } (2xPbCl_2 + xCsCl) - (1-3x)\bar{M}Cl)]\ (700°C)}$

## 3.3 THE RECIPROCAL SYSTEMS $Cd^{2+}$, $Na^{+}$, $Br^{-}$, $Cl^{-}$

a) Pure $CdBr_2$

The e.m.f. $E^{o}$, for the formation cell:

Sn,Cd/pure $CdBr_2$/C, $Br_2$,

was measured over the temperature range 600-800°C. The results are recorded in Table 3.63 and are illustrated, together with the values obtained by other workers, in fig. 3.54. The present results lie between those of Lantratov and Shevlyakova[1] and Weber[2] on the one hand and Lorenz and Kaufler[3] on the other. The temperature coefficient of the e.m.f. is more closely related to the former group. The rather large discrepancy in $E^{o}$, could well be due to the solubility of the molten cadmium metal electrode in the melt. In this work, the solubility was depressed by alloying the pure cadmium with A.R. grade tin (see Section 2.5i). According to Richards[4], the solubility of the metal from an equimolar alloy is about 9 mole % in pure $CdCl_2$, but falls to approximately 1 mole % in the mixtures $CdCl_2$ + NaCl and $CdCl_2$ + KCl.

The present results conform well to a linear relationship between e.m.f. E, and the temperature t°C; for the cell:

Sn, Cd/pure $CdBr_2$/C, $Br_2$,

$E = 1.3981 - (5.645 \times 10^{-4})t$

---

1. Lantratov and Shevlyakova: Zhur. Priklad. Khim., 34 1065 (1961)
2. Weber: Z anorg. u allgem. Chem., 21 305 (1899)
3. Lorenz and Kaufler: quoted by Lantratov and Shevlyakova (see ref.1)
4. Richards: Ph.D. thesis, University of New Zealand (1956)

where the mean deviation of the experimental points is 0.2 millivolts.

Thermodynamic data for pure $CdBr_2$ are presented in Table 3.64.

b) The system $CdBr_2$-NaCl

The variations of e.m.f. with temperature for the cells:

$$Sn, Cd/CdBr_2(N_1) + NaCl(N_2)/C, Br_2,$$

are listed in Table 3.65. The equations to the lines of best fit are recorded in Table 3.66 and illustrated in fig. 3.55. Isotherms of e.m.f. vs. mole fraction of $CdBr_2$ are also shown in fig. 3.56.

Activities and activity coefficients for $CdBr_2$ are presented in Table 3.67 and fig. 3.57, together with the ideal Temkin activities. Values for the other component were calculated from the Gibbs-Duhem equation and are shown in Table 3.68 and fig. 3.58. Errors in $a_{CdBr_2}$ are less than $\pm 0.003$ units for mixtures below 0.65 mole fraction $CdBr_2$ but above this value the error steadily increases to a maximum of $\pm 0.034$ units at 0.90 mole fraction $CdBr_2$.

In the reciprocal systems, ideal thermodynamic quantities cannot be calculated with any degree of certainty. For the binary systems, ideal properties can be obtained, by assuming the melt to be completely dissociated into non-interacting ions. For reciprocal systems, an exchange equilibrium must be postulated, which is associated with an energy change depending on the equilibrium reaction:

$$CdBr_2 + 2NaCl \overset{K}{\rightleftharpoons} CdCl_2 + 2NaBr.$$

Because of the difficulty in estimating the equilibrium constant, ideal thermodynamic functions cannot be obtained simply and hence excess thermodynamic functions are not accessible. Partial molar quantities for $CdBr_2$ are shown in Table 3.69 and in figs. 3.59 and 3.60. Integral free energies for the system $CdBr_2$-NaCl, are listed in Table 3.70 and drawn in fig. 3.59. Errors in the thermodynamic quantities are of the same order of magnitude as those for the binary lead bromide-alkali metal bromide systems.

c) The system $CdCl_2$-NaBr

Values of e.m.f. over a 170°C temperature range for the cells:

$$Sn, Cd/CdCl_2(N_1) + NaBr(N_2)/C, Br_2,$$

are given in Table 3.71. The cell reaction is the formation of $CdBr_2$ from its elements. As the exchange reaction made it difficult to interpret the thermodynamic quantities with respect to the mole fraction of $CdBr_2$ (see Section 4C.1), these properties were discussed with reference to the mole fraction of cadmium chloride. Equations to the lines of best fit are given in Table 3.72 and are illustrated in fig.3.61. E.m.f. isotherms as functions of composition, are shown in fig. 3.62.

The activities and activity coefficients of $CdBr_2$ at three temperatures are presented in Table 3.73 and are plotted in fig. 3.63. Because of the relatively large differences between E and $E^\circ$, as compared to the system $CdBr_2$-NaCl, errors in the activity were less than $\pm$ 0.0015 units over the whole composition range. Because of the

exchange reaction and the associated difficulties mentioned above, the activity and activity coefficient of sodium chloride could not be estimated from the Gibbs-Duhem equation.

Partial molar thermodynamic quantities for $CdBr_2$ as functions of the mole fraction of $CdCl_2$, are summarized in Table 3.74. The errors in these values are of the same magnitude as in the system $CdBr_2$-NaCl.

TABLE 3.63

Values of e.m.f. and temperature for the cell:

Cd/pure $CdBr_2$/C, $Br_2$

| temperature (°C) | e.m.f. (volts) | △E (mv.) | temperature (°C) | e.m.f. (volts) | △E (mv.) |
|---|---|---|---|---|---|
| 612.8 | 1.0525 | +0.3 | 700.1 | 1.0032 | +0.3 |
| 636.4 | 1.0384 | -0.5 | 717.8 | 0.9931 | +0.1 |
| 664.5 | 1.0230 | 0.0 | 741.3 | 0.9797 | +0.1 |
| 680.0 | 1.0142 | 0.0 | 775.1 | 0.9601 | -0.5 |
| 691.0 | 1.0079 | -0.1 | 802.1 | 0.9453 | 0.0 |

Equation to line : $E = 1.3981 - (5.645 \times 10^{-4})t$

Mean deviation : 0.2 mv.

TABLE 3.64

Thermodynamic properties of pure $CdBr_2$

| temperature (°C) | $\Delta G^\circ$ (K cal/mole) | $\Delta S^\circ$ (cal/deg/mole) | $\Delta H^\circ$ (K cal/mole) |
|---|---|---|---|
| 600 | -48.86 | | |
| 700 | -46.26 | -26.04 | -71.59 |
| 800 | -43.66 | | |

TABLE 3.65

Values of e.m.f. and temperature for the formation cells:

$Cd/CdBr_2(N_1) + NaCl(N_2)/C, Br_2$

| composition (m.f.$CdBr_2$) | temp. (°C) | e.m.f. (volts) | Δ E (mv.) | temp. (°C) | e.m.f. (volts) | Δ E (mv.) |
|---|---|---|---|---|---|---|
| 0.901 | 607.8 | 1.0614 | -1.5 | 711.6 | 1.0017 | -0.9 |
| | 634.0 | 1.0474 | -0.3 | 736.4 | 0.9863 | -1.9 |
| | 661.0 | 1.0343 | +2.3 | 759.1 | 0.9765 | +1.5 |
| | 687.0 | 1.0193 | +3.6 | 787.2 | 0.9574 | -1.3 |
| 0.790 | 603.2 | 1.0662 | +0.3 | 713.0 | 1.0085 | +2.2 |
| | 627.8 | 1.0509 | -1.7 | 738.2 | 0.9914 | -1.3 |
| | 654.0 | 1.0392 | +0.9 | 765.1 | 0.9786 | +0.5 |
| | 680.2 | 1.0237 | -0.4 | 789.8 | 0.9640 | -0.7 |
| 0.723 | 604.6 | 1.0851 | 0.0 | 712.2 | 1.0216 | +0.5 |
| | 631.2 | 1.0686 | -0.7 | 738.8 | 1.0045 | -0.8 |
| | 658.1 | 1.0528 | +0.5 | 762.1 | 0.9912 | -0.2 |
| | 687.9 | 1.0368 | +1.3 | 789.0 | 0.9753 | -0.1 |
| 0.657 | 613.8 | 1.0927 | -0.3 | 717.0 | 1.0377 | +0.5 |
| | 641.0 | 1.0783 | 0.0 | 743.2 | 1.0219 | -1.7 |
| | 666.6 | 1.0647 | +0.3 | 770.1 | 1.0091 | +0.6 |
| | 691.6 | 1.0515 | +0.6 | 797.7 | 0.9932 | -0.4 |
| 0.561 | 615.0 | 1.0978 | 0.0 | 687.9 | 1.0629 | +0.1 |
| | 640.4 | 1.0857 | +0.1 | 713.0 | 1.0515 | +0.8 |
| | 662.8 | 1.0747 | -0.2 | 742.0 | 1.0362 | -0.6 |
| 0.449 | 624.5 | 1.1186 | -0.1 | 723.0 | 1.0758 | +1.5 |
| | 651.1 | 1.1059 | -0.8 | 749.9 | 1.0620 | -0.1 |
| | 675.0 | 1.0959 | 0.0 | 778.1 | 1.0494 | 0.0 |
| | 698.6 | 1.0854 | +0.1 | 802.5 | 1.0382 | -0.2 |

Table 3.65 (contd.)

| composition (m.f.$CdBr_2$) | temp. (°C) | e.m.f. (volts) | $\Delta E$ (mv.) | temp. (°C) | e.m.f. (volts) | $\Delta E$ (mv.) |
|---|---|---|---|---|---|---|
| 0.348 | 636.6 | 1.1377 | -0.6 | 733.0 | 1.0996 | +0.8 |
| | 660.0 | 1.1284 | -0.3 | 759.0 | 1.0875 | -0.7 |
| | 685.6 | 1.1188 | +0.6 | 783.1 | 1.0782 | -0.1 |
| | 707.8 | 1.1094 | +0.3 | 807.5 | 1.0683 | 0.0 |
| 0.247 | 689.7 | 1.1486 | 0.0 | 764.6 | 1.1246 | -0.6 |
| | 713.3 | 1.1403 | -0.7 | 778.5 | 1.1203 | +0.8 |
| | 738.2 | 1.1320 | +0.5 | | | |

TABLE 3.66

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:

$Cd/CdBr_2(N_1) + NaCl(N_2)/C, Br_2$

| composition (m.f.$CdBr_2$) | e.m.f. at temperature t°C (volts) | mean deviation |
|---|---|---|
| 0.901 | $1.4160 - (5.809 \times 10^{-4})t$ | 1.6 |
| 0.790 | $1.3932 - (5.426 \times 10^{-4})t$ | 1.0 |
| 0.723 | $1.4445 - (5.945 \times 10^{-4})t$ | 0.5 |
| 0.657 | $1.4246 - (5.403 \times 10^{-4})t$ | 0.5 |
| 0.561 | $1.3932 - (4.803 \times 10^{-4})t$ | 0.3 |
| 0.449 | $1.4007 - (4.515 \times 10^{-4})t$ | 0.4 |
| 0.348 | $1.3989 - (4.094 \times 10^{-4})t$ | 0.5 |
| 0.247 | $1.3747 - (3.278 \times 10^{-4})t$ | 0.5 |

TABLE 3.67

Value of activity and activity coefficient of $CdBr_2$ at different compositions (mole fraction $CdBr_2$) for the system $CdBr_2$-NaCl

| composition (m.f.$CdBr_2$) | activity $CdBr_2$ | | | Error $a_{CdBr_2}$ | activity coeff. $CdBr_2$ | | |
|---|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | (700°) | 600°C | 700°C | 800°C |
| 1.000 | 1.000 | 1.000 | 1.000 | | 1.000 | 1.000 | 1.000 |
| 0.901 | 0.8063 | 0.9015 | 0.8565 | ±0.034 | 0.997 | 1.058 | 1.114 |
| 0.790 | 0.8042 | 0.7617 | 0.7787 | ±0.019 | 1.306 | 1.265 | 1.237 |
| 0.723 | 0.4703 | 0.6163 | 0.5459 | ±0.007 | 0.924 | 1.072 | 1.211 |
| 0.657 | 0.3364 | 0.3709 | 0.3546 | <±0.003 | 0.815 | 0.859 | 0.899 |
| 0.651 | 0.2978 | 0.2590 | 0.2754 | " | 1.027 | 0.950 | 0.893 |
| 0.449 | 0.1540 | 0.1340 | 0.1427 | " | 0.892 | 0.826 | 0.776 |
| 0.348 | 0.0826 | 0.0673 | 0.0738 | " | 0.888 | 0.794 | 0.724 |
| 0.247 | 0.0428 | 0.0277 | 0.0337 | " | 1.106 | 0.871 | 0.716 |

TABLE 3.68

Value of the activity and activity coefficient of NaCl (700°C) at different compositions in the system $CdBr_2$-NaCl

| composition (m.f.$CdBr_2$) | activity NaCl (700°C) | ideal Temkin activity | activity coeff. NaCl (700°C) |
|---|---|---|---|
| 0.900 | 0.010 | 0.005 | 1.995 |
| 0.889 | 0.013 | 0.007 | 1.824 |
| 0.875 | 0.014 | 0.009 | 1.596 |
| 0.857 | 0.013 | 0.010 | 1.334 |
| 0.833 | 0.016 | 0.015 | 1.081 |
| 0.800 | 0.019 | 0.022 | 0.855 |
| 0.750 | 0.026 | 0.037 | 0.692 |
| 0.706 | 0.034 | 0.052 | 0.656 |
| 0.667 | 0.046 | 0.068 | 0.673 |
| 0.600 | 0.072 | 0.100 | 0.718 |
| 0.500 | 0.124 | 0.167 | 0.745 |
| 0.429 | 0.178 | 0.230 | 0.773 |
| 0.333 | 0.274 | 0.335 | 0.819 |
| 0.200 | 0.475 | 0.534 | 0.889 |

TABLE 3.69

Partial molar thermodynamic functions of $CdBr_2$ at different compositions (mole fractions $CdBr_2$) in the system $CdBr_2$-NaCl

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | 700°C | | | | |
| mole fraction $CdBr_2$ | 1.000 | 0.901 | 0.790 | 0.723 | 0.657 | 0.561 | 0.449 | 0.348 | 0.247 |
| $\Delta G_1$ (K cal/mole) | -46.26 | -46.56 | -46.74 | -47.43 | -48.26 | -48.75 | -50.03 | -51.30 | -52.82 |
| $\Delta S_1$ (cal/deg/mole) | -26.04 | -26.79 | -25.03 | -27.42 | -24.92 | -22.15 | -20.83 | -18.88 | -15.12 |
| $\Delta H_1$ (K cal/mole) | -71.59 | -72.63 | -71.09 | -74.11 | -72.51 | -70.31 | -70.29 | -69.68 | -67.53 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.30 | - 0.48 | - 1.17 | - 2.01 | - 2.50 | - 3.77 | - 5.05 | - 6.56 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | - 0.76 | + 1.01 | - 1.38 | + 1.12 | + 3.88 | + 5.21 | + 7.15 | +10.92 |
| $\Delta \bar{H}_1$ (K cal/mole) | | - 1.03 | + 0.50 | - 2.51 | - 0.92 | + 1.29 | + 1.31 | + 1.92 | + 4.06 |
| | | | | | 600°C | | | | |
| $\Delta G_1$ (K cal/mole) | -48.86 | -49.24 | -49.24 | -50.17 | -50.76 | -50.97 | -52.11 | -53.20 | -54.33 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.37 | - 0.38 | - 1.31 | - 1.89 | - 2.10 | - 3.25 | - 4.33 | - 5.47 |
| | | | | | 800°C | | | | |
| $\Delta G_1$ (K cal/mole) | -43.66 | -43.88 | -44.24 | -44.69 | -45.77 | -46.54 | -47.95 | -49.42 | -51.51 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 0.22 | - 0.58 | - 1.03 | - 2.12 | - 2.88 | - 4.29 | - 5.76 | - 7.66 |

TABLE 3.70

Integral free energy for the system $CdBr_2$-NaCl as a function of composition (700°C)

| composition (m.f.$CdBr_2$) | $\triangle G$ (K cal/mole) | composition (m.f.$CdBr_2$) | $\triangle G$ (K cal/mole) | composition (m.f.$CdBr_2$) | $\triangle G$ (K cal/mole) |
|---|---|---|---|---|---|
| 0.900 | -1.427 | 0.525 | -3.990 | 0.150 | -3.230 |
| 0.825 | -2.226 | 0.450 | -4.114 | 0.100 | -2.727 |
| 0.750 | -2.948 | 0.375 | -4.081 | 0.050 | -1.777 |
| 0.675 | -3.452 | 0.300 | -3.900 | | |
| 0.600 | -3.760 | 0.225 | -3.681 | | |

TABLE 3.71

Values of e.m.f. and temperature for the formation cells:

$Cd/CdCl_2(N_1) + NaBr(N_2)/C, Br_2$

| composition (m.f.$CdCl_2$) | temp. (°C) | e.m.f. (volts) | △E (mv.) | temp. (°C) | e.m.f. (volts) | △E (mv.) |
|---|---|---|---|---|---|---|
| 0.918 | 600.0 | 1.1576 | -0.2 | 699.1 | 1.1074 | +0.3 |
| | 626.6 | 1.1440 | -0.2 | 726.5 | 1.0929 | -0.2 |
| | 649.6 | 1.1319 | -0.5 | 748.3 | 1.0819 | 0.0 |
| | 673.0 | 1.1210 | +0.5 | 771.0 | 1.0700 | -0.3 |
| 0.854 | 593.6 | 1.1620 | +1.0 | 728.5 | 1.0864 | +0.3 |
| | 616.0 | 1.1474 | -1.1 | 757.1 | 1.0696 | -0.7 |
| | 640.2 | 1.1346 | -0.5 | 790.8 | 1.0521 | +0.5 |
| | 699.0 | 1.1026 | +0.1 | | | |
| 0.820 | 591.5 | 1.1603 | +0.3 | 688.5 | 1.1038 | -1.6 |
| | 614.6 | 1.1461 | -0.9 | 712.6 | 1.0925 | +0.7 |
| | 639.1 | 1.1347 | +1.5 | 736.6 | 1.0786 | +0.3 |
| | 664.5 | 1.1188 | -0.1 | 762.5 | 1.0636 | -0.1 |
| 0.741 | 589.6 | 1.1613 | -0.1 | 683.5 | 1.1076 | +0.3 |
| | 615.4 | 1.1470 | +0.5 | 710.0 | 1.0916 | -0.5 |
| | 638.5 | 1.1325 | -0.7 | 736.0 | 1.0782 | +1.1 |
| | 660.4 | 1.1202 | -0.4 | 762.1 | 1.0618 | -0.3 |
| 0.564 | 588.0 | 1.1623 | -0.4 | 681.2 | 1.1151 | +0.1 |
| | 613.0 | 1.1502 | +0.3 | 706.0 | 1.1024 | +0.2 |
| | 635.4 | 1.1383 | -0.1 | 731.5 | 1.0888 | -0.4 |
| | 659.8 | 1.1255 | -0.4 | 758.9 | 1.0755 | +0.4 |
| 0.450 | 590.9 | 1.1618 | +0.3 | 685.0 | 1.1176 | -0.2 |
| | 615.0 | 1.1506 | +0.1 | 711.0 | 1.1047 | -0.9 |
| | 635.8 | 1.1416 | -0.6 | 736.0 | 1.0944 | +0.6 |
| | 664.5 | 1.1279 | +0.4 | 752.1 | 1.0862 | 0.0 |

Table 3.71 (contd.)

| composition (m.f.$CdCl_2$) | temp. (°C) | e.m.f. (volts) | $\Delta E$ (mv.) | temp. (°C) | e.m.f. (volts) | $\Delta E$ (mv.) |
|---|---|---|---|---|---|---|
| 0.350 | 588.4 | 1.1725 | -0.9 | 684.7 | 1.1288 | -1.4 |
| | 613.0 | 1.1633 | +0.9 | 708.7 | 1.1190 | -0.4 |
| | 635.0 | 1.1533 | +0.8 | 729.8 | 1.1103 | +0.4 |
| | 658.7 | 1.1424 | +0.5 | | | |
| 0.248 | 601.8 | 1.1756 | -0.3 | 697.0 | 1.1397 | +0.3 |
| | 625.7 | 1.1664 | +0.1 | 722.0 | 1.1300 | 0.0 |
| | 648.2 | 1.1577 | -0.1 | 747.2 | 1.1204 | -0.1 |
| | 673.2 | 1.1476 | -0.8 | 778.5 | 1.1090 | +0.3 |
| 0.124 | 655.0 | 1.1849 | +0.3 | 747.4 | 1.1511 | -0.1 |
| | 678.2 | 1.1768 | +0.6 | 771.0 | 1.1432 | +0.5 |
| | 702.0 | 1.1659 | -1.7 | 795.0 | 1.1348 | +0.8 |
| | 723.4 | 1.1602 | +0.3 | | | |

TABLE 3.72

Relationship between e.m.f. and temperature from the lines of best fit for the formation cells:

$Cd/CdCl_2(N_1) + NaBr(N_2)/C, Br_2$

| composition (m.f.$CdCl_2$) | e.m.f. at temperature t°C (volts) | mean deviation |
|---|---|---|
| 0.918 | $1.4651 - (5.121 \times 10^{-4})t$ | 0.3 |
| 0.854 | $1.4903 - (5.548 \times 10^{-4})t$ | 0.6 |
| 0.820 | $1.4931 - (5.631 \times 10^{-4})t$ | 0.7 |
| 0.741 | $1.5007 - (5.755 \times 10^{-4})t$ | 0.5 |
| 0.564 | $1.4640 - (5.124 \times 10^{-4})t$ | 0.3 |
| 0.450 | $1.4401 - (4.705 \times 10^{-4})t$ | 0.4 |
| 0.350 | $1.4377 - (4.491 \times 10^{-4})t$ | 0.7 |
| 0.248 | $1.4020 - (3.767 \times 10^{-4})t$ | 0.3 |
| 0.124 | $1.4212 - (3.612 \times 10^{-4})t$ | 0.6 |

## TABLE 3.73

**Values of activity and activity coefficient of $CdBr_2$ at different compositions (mole fractions $CdCl_2$) for the system $CdCl_2$-NaBr**

| composition (m.f.$CdCl_2$) | activity CdBr2 | | | Error $a_{CdBr_2}$ | activity coeff. $CdBr_2$ | | |
|---|---|---|---|---|---|---|---|
| | 600°C | 700°C | 800°C | (700°C) | 600°C | 700°C | 800°C |
| 0.918 | 0.0733 | 0.0843 | 0.0951 | $<\pm$0.0015 | 43.117 | 49.588 | 55.941 |
| 0.854 | 0.0740 | 0.0946 | 0.1152 | " | 13.962 | 17.849 | 21.730 |
| 0.820 | 0.0785 | 0.1014 | 0.1253 | " | 9.812 | 12.675 | 15.660 |
| 0.741 | 0.0780 | 0.1041 | 0.1317 | " | 4.756 | 6.347 | 8.030 |
| 0.564 | 0.0757 | 0.0871 | 0.0977 | " | 1.728 | 1.989 | 2.231 |
| 0.450 | 0.0733 | 0.0766 | 0.0794 | " | 1.133 | 1.184 | 1.227 |
| 0.350 | 0.0556 | 0.0566 | 0.0578 | " | 0.686 | 0.698 | 0.713 |
| 0.248 | 0.0451 | 0.0396 | 0.0358 | " | 0.501 | 0.440 | 0.398 |
| 0.124 | 0.0212 | 0.0194 | 0.0181 | " | 0.282 | 0.258 | 0.240 |

## TABLE 3.74

**Partial molar thermodynamic functions of $CdBr_2$ at different compositions (mole fractions $CdCl_2$) in the system $CdCl_2$-NaBr**

| mole fraction $CdCl_2$ | pure $CdBr_2$ | 0.918 | 0.854 | 0.820 | 0.741 | 0.564 | 0.450 | 0.350 | 0.248 | 0.124 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 700°C | | | | | |
| $\Delta G_1$ (K cal/mole) | -46.26 | -51.04 | -50.82 | -50.69 | -50.64 | -50.98 | -51.23 | -51.81 | -52.50 | -53.89 |
| $\Delta S_1$ (cal/deg/mole) | -26.04 | -23.62 | -25.59 | -25.97 | -26.54 | -23.63 | -21.70 | -20.71 | -17.38 | -16.66 |
| $\Delta H_1$ (K cal/mole) | -71.59 | -74.02 | -75.72 | -75.96 | -76.46 | -73.98 | -72.35 | -71.97 | -69.41 | -70.10 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 4.78 | - 4.57 | - 4.43 | - 4.38 | - 4.72 | - 4.97 | - 4.55 | - 6.25 | - 7.63 |
| $\Delta \bar{S}_1$ (cal/deg/mole) | | + 2.42 | + 0.45 | + 0.07 | - 0.51 | + 2.40 | + 4.34 | + 5.32 | + 8.66 | + 9.38 |
| $\Delta \bar{H}_1$ (K cal/mole) | | - 2.43 | - 4.13 | - 4.36 | - 4.87 | - 2.38 | - 0.75 | - 0.37 | + 2.19 | + 1.49 |
| | | | | | 600°C | | | | | |
| $\Delta G_1$ (K cal/mole) | -48.86 | -53.40 | -53.38 | -53.28 | -53.29 | -53.35 | -53.40 | -53.88 | -54.24 | -55.56 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 4.54 | - 4.52 | - 4.42 | - 4.43 | - 4.48 | - 4.54 | - 5.02 | - 5.38 | - 6.69 |
| | | | | | 800°C | | | | | |
| $\Delta G_1$ (K cal/mole) | -43.66 | -48.68 | -48.27 | -48.09 | -47.98 | -48.62 | -49.06 | -49.74 | -50.76 | -52.22 |
| $\Delta \bar{G}_1$ (K cal/mole) | | - 5.02 | - 4.61 | - 4.43 | - 4.33 | - 4.96 | - 5.41 | - 6.08 | - 7.11 | - 8.57 |

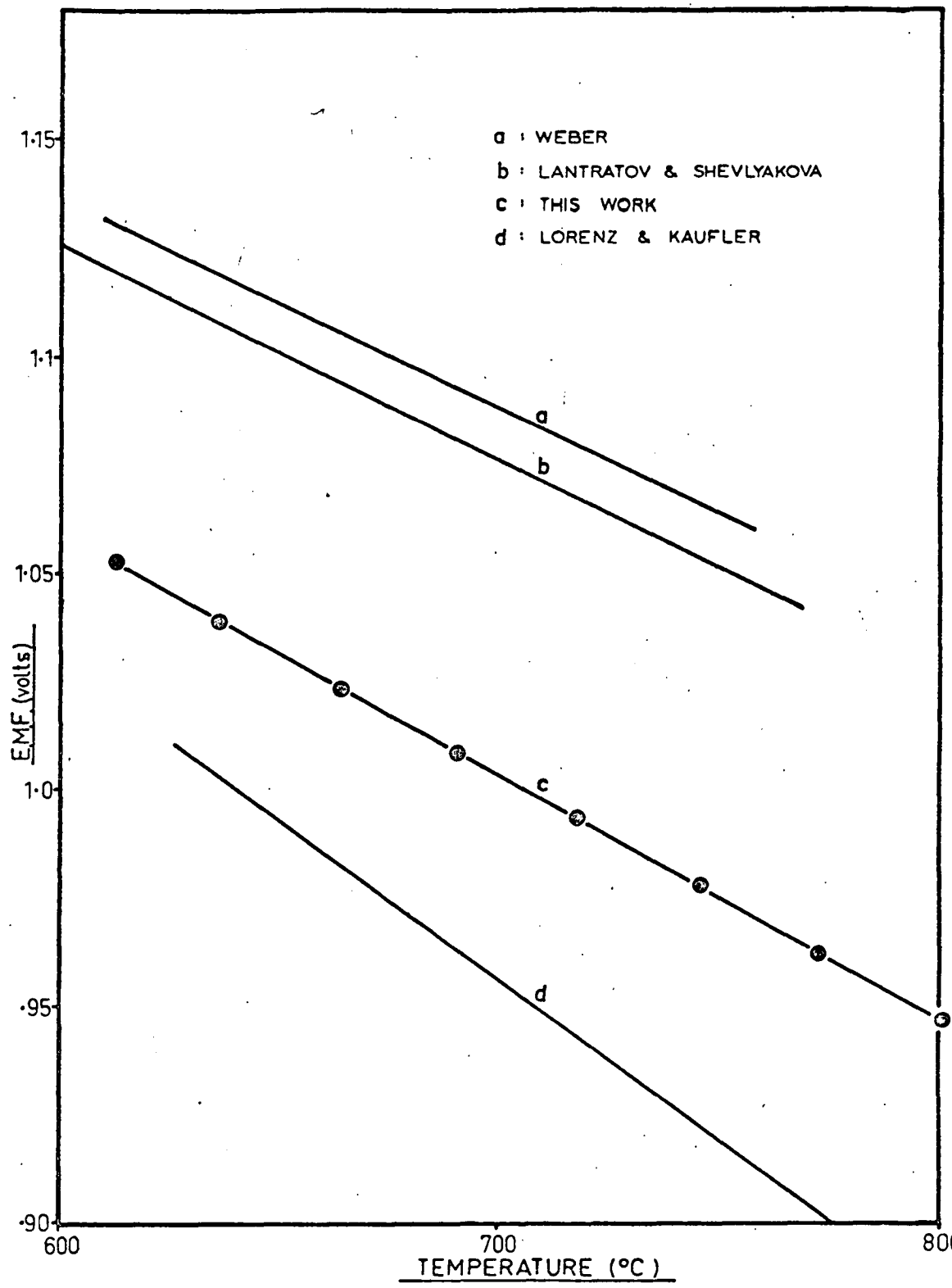



FIG. 3·54 E° PURE $CdBr_2$ vs TEMPERATURE

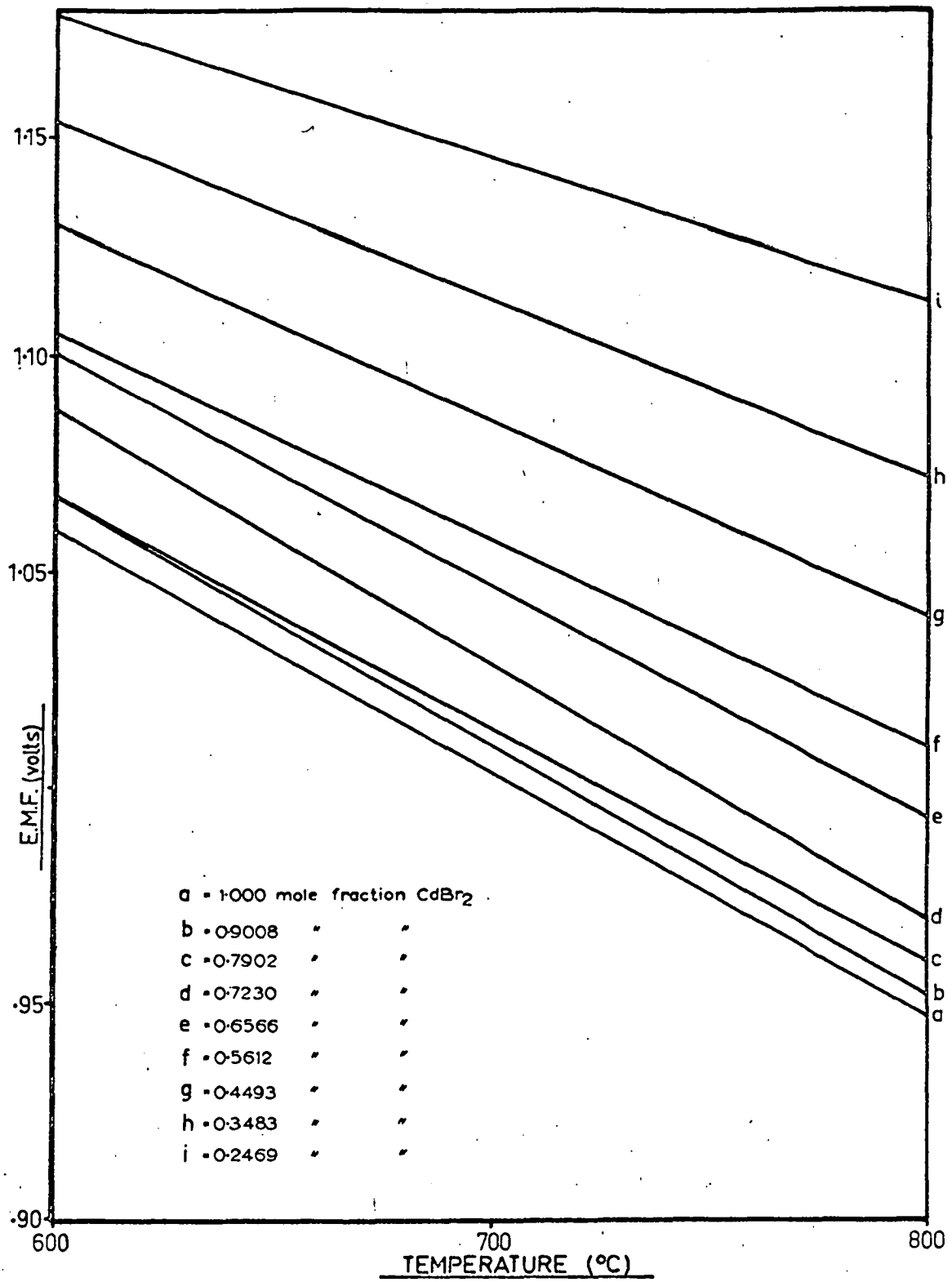



FIG. 3·55

SYSTEM $CdBr_2$–NaCl

E.M.F. vs TEMPERATURE

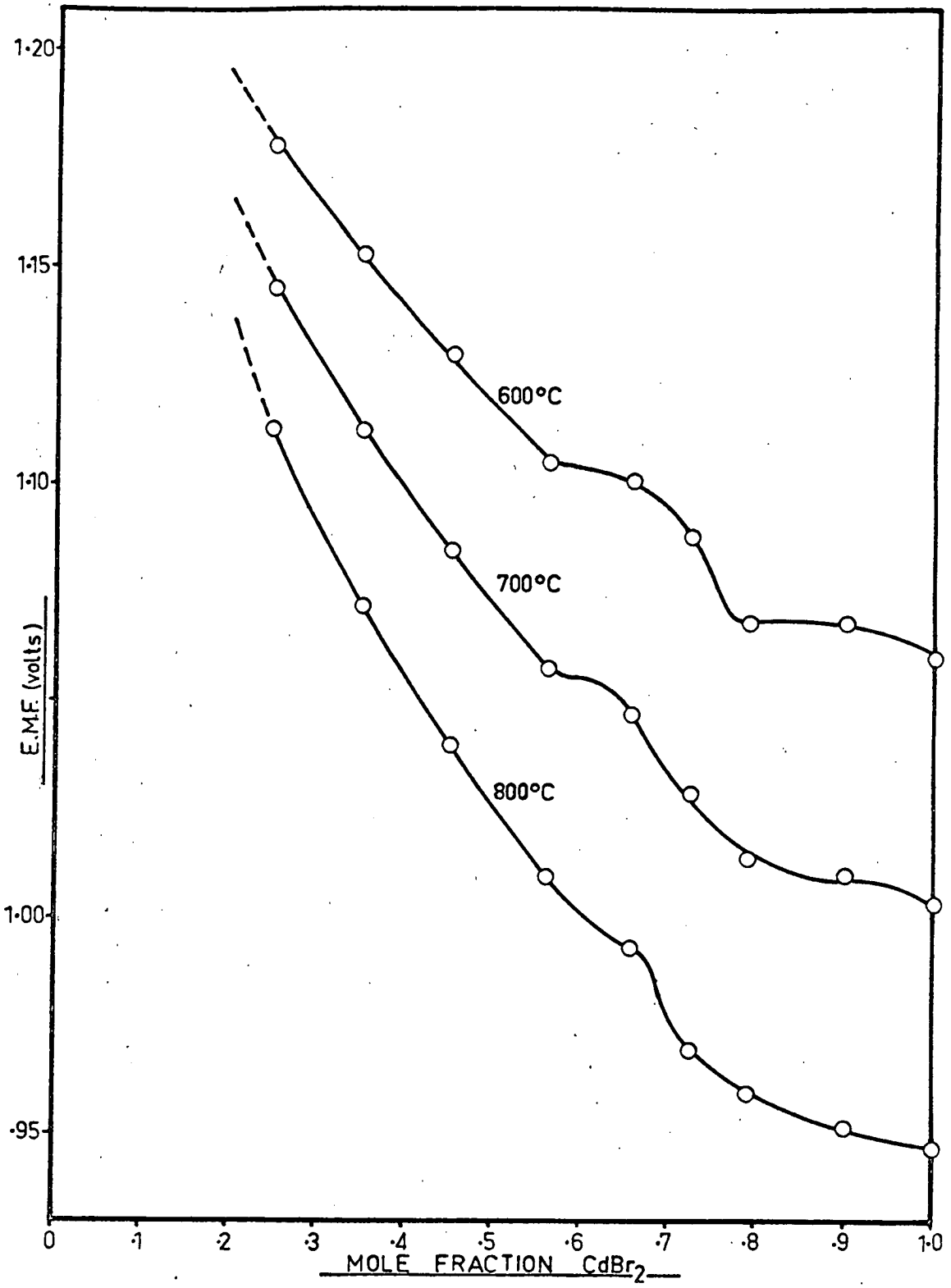



FIG. 3·56

SYSTEM $CdBr_2$—NaCl

E.M.F. vs COMPOSITION

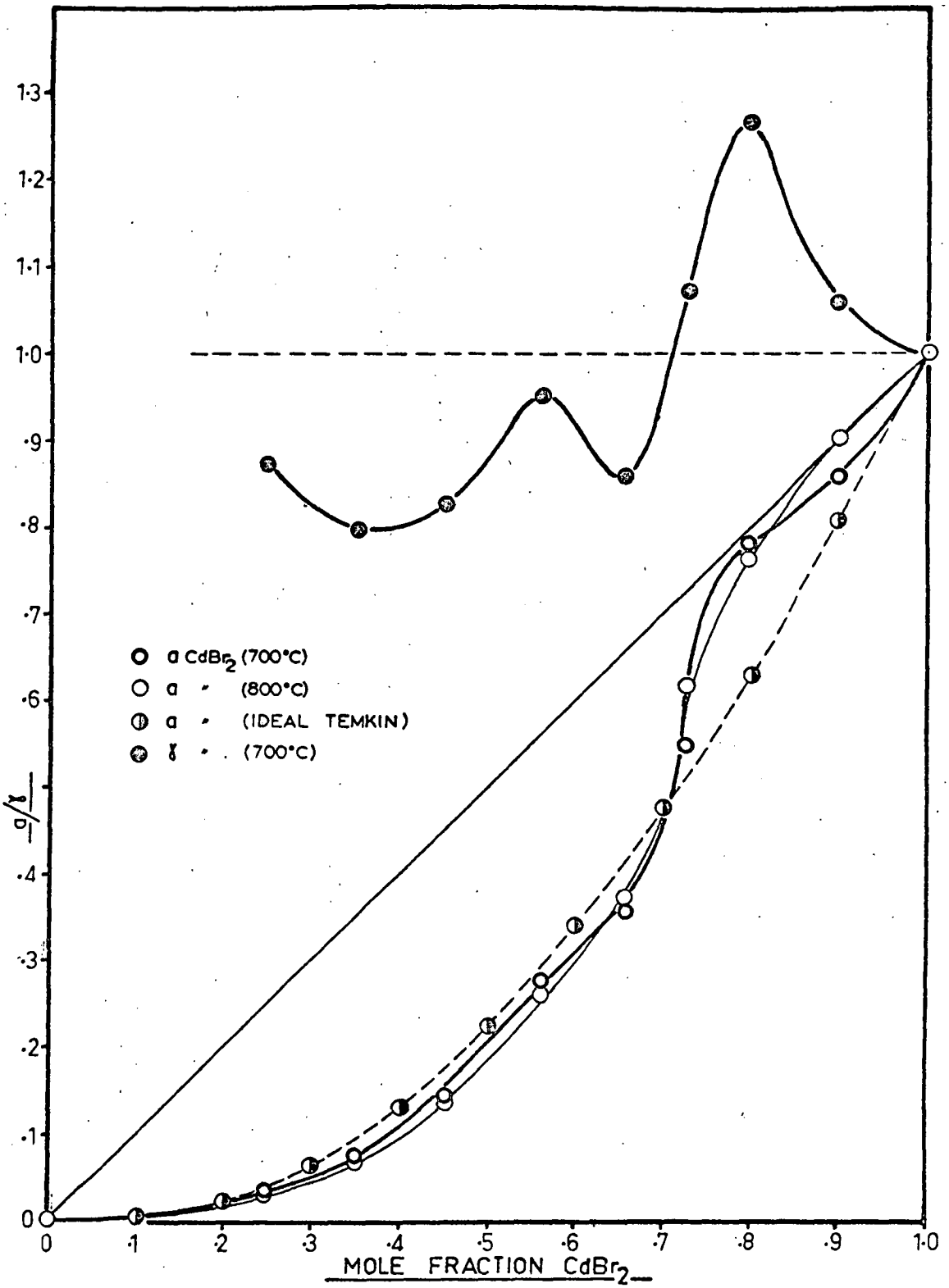



FIG. 357 SYSTEM $CdBr_2$–NaCl

ACTIVITY & ACTIVITY COEFF $CdBr_2$ vs COMPOSITION

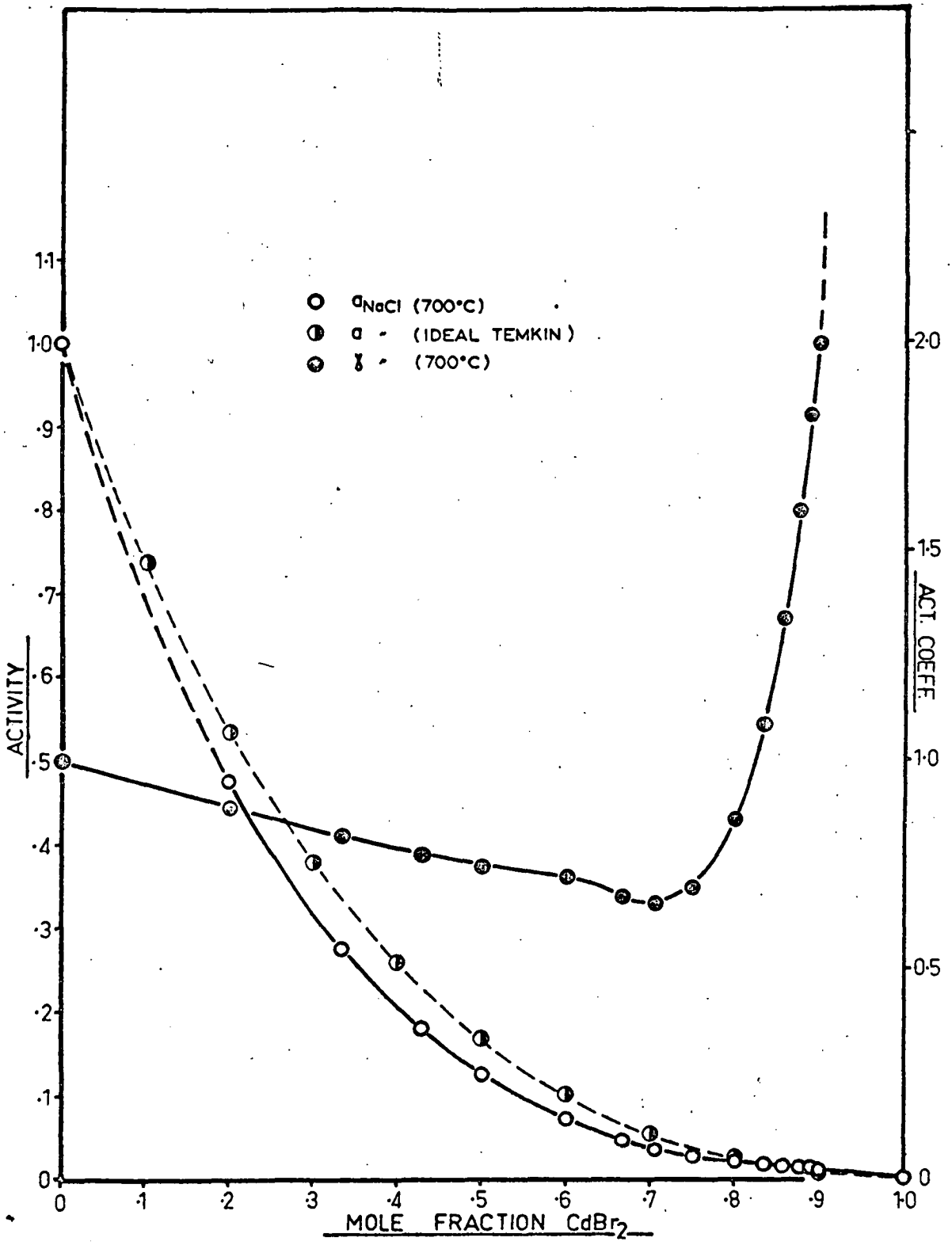



FIG. 3·58 SYSTEM $CdBr_2$–NaCl

ACTIVITY & ACTIVITY COEFF. NaCl vs COMPOSITION

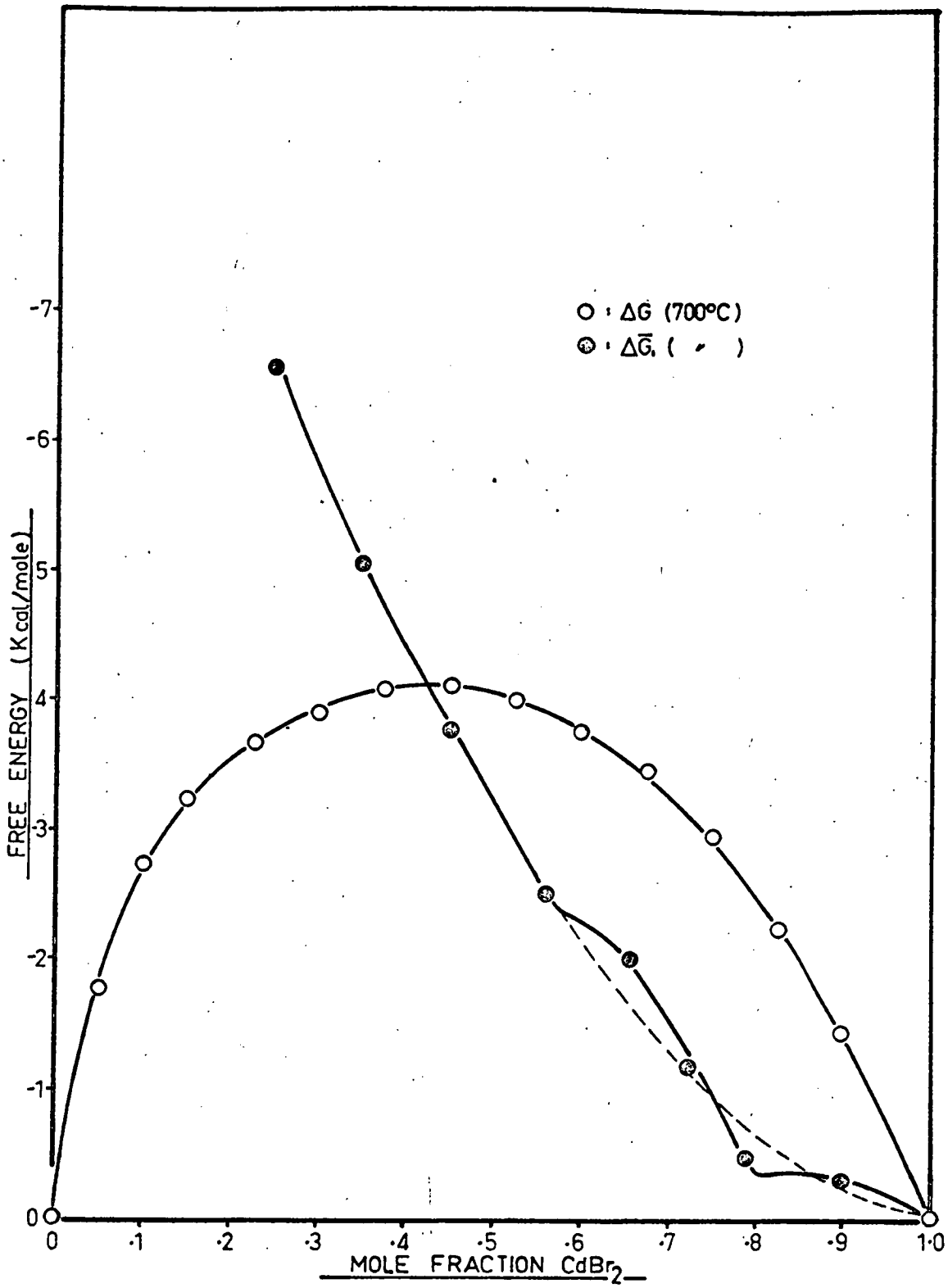



FIG. 3·59 SYSTEM $CdBr_2$–NaCl

PARTIAL & INTEGRAL FREE ENERGY $CdBr_2$ vs COMPOSITION

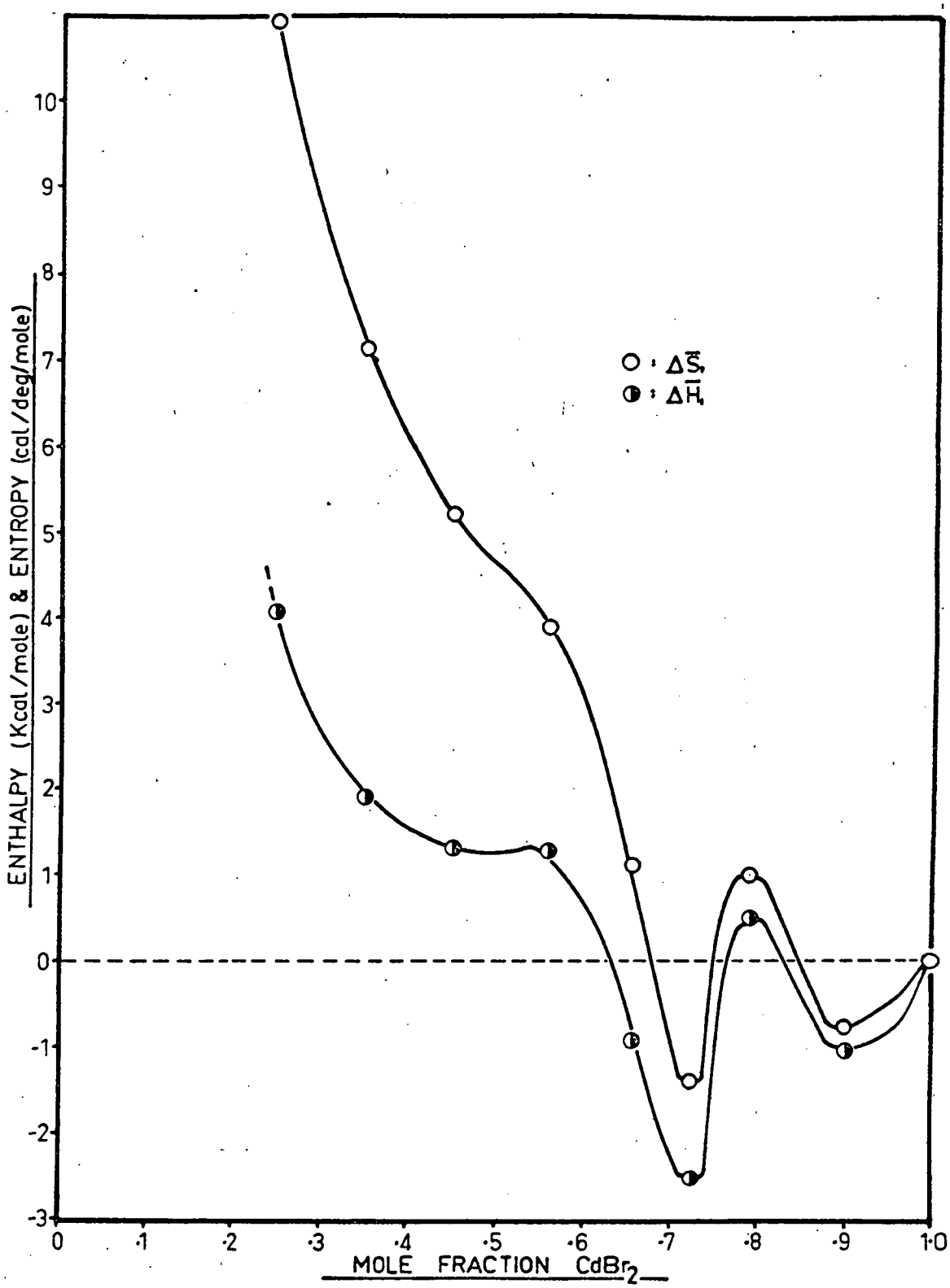



FIG. 3·60

SYSTEM $CdBr_2$ — NaCl

PARTIAL THERMODYNAMIC FUNCTIONS $CdBr_2$ (700°C)

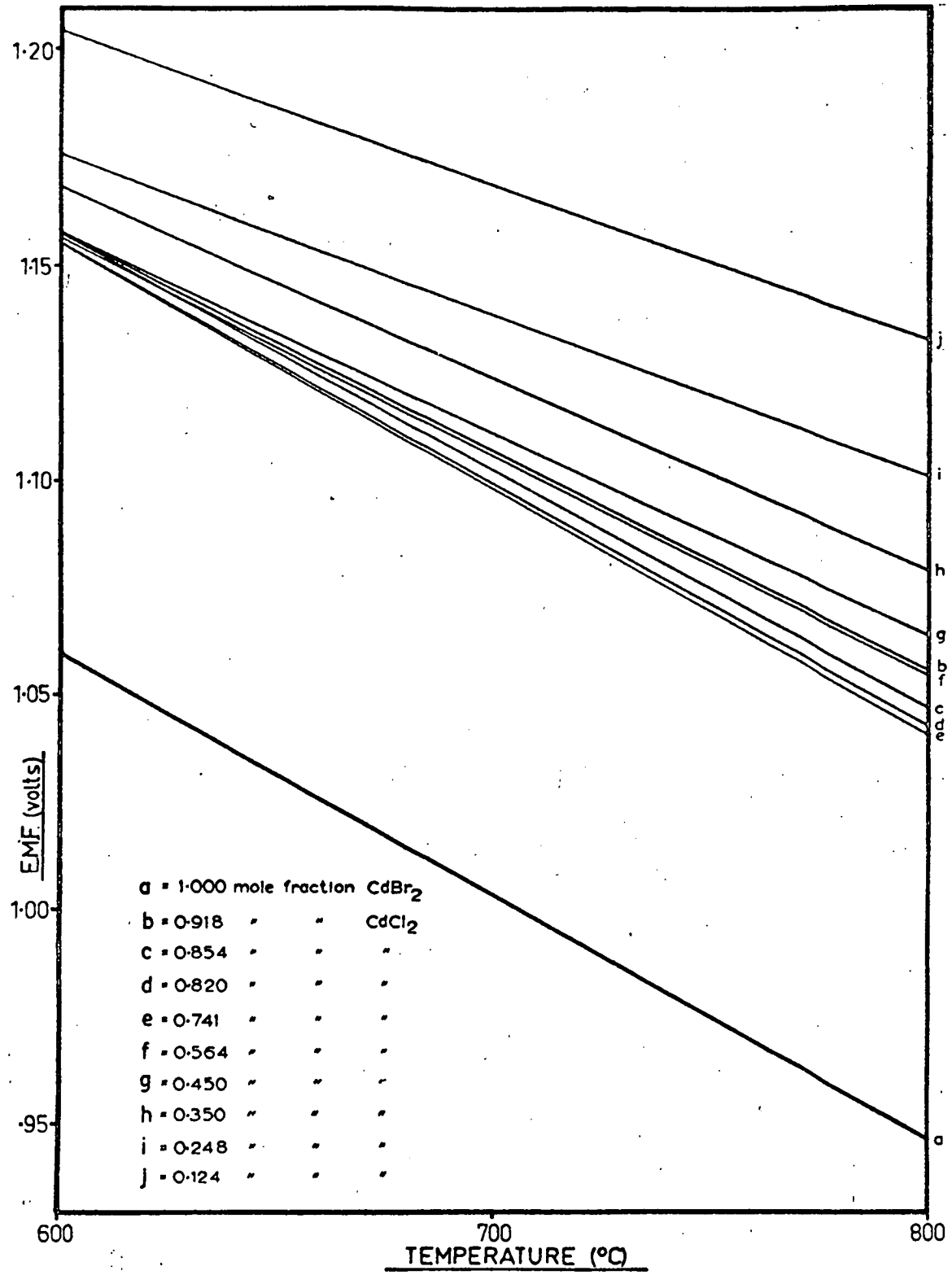



FIG. 3·61

SYSTEM $CdCl_2$ — NaBr

E.M.F. vs TEMPERATURE

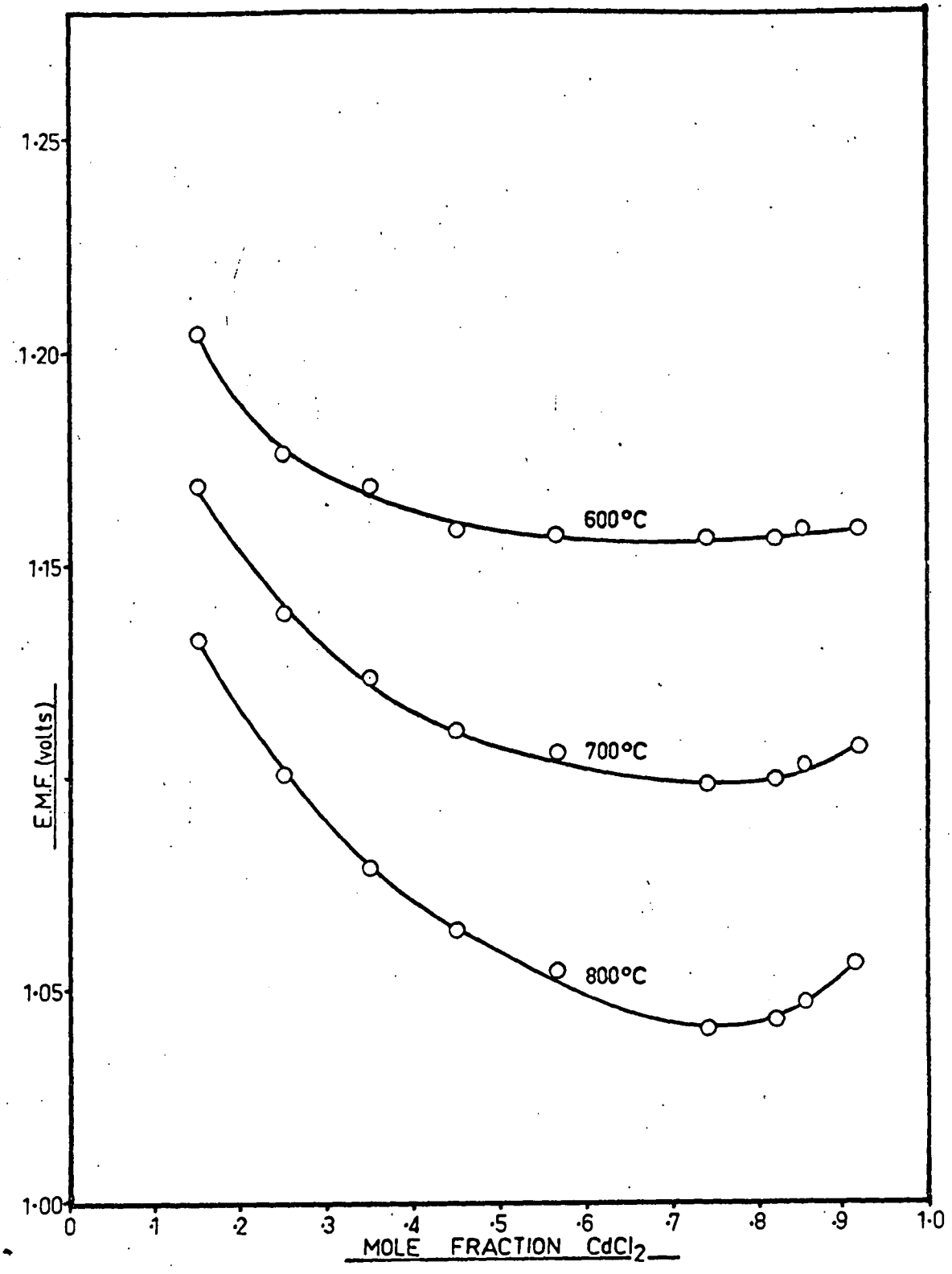



FIG. 3·62

SYSTEM $CdCl_2$–NaBr

E.M.F. vs COMPOSITION

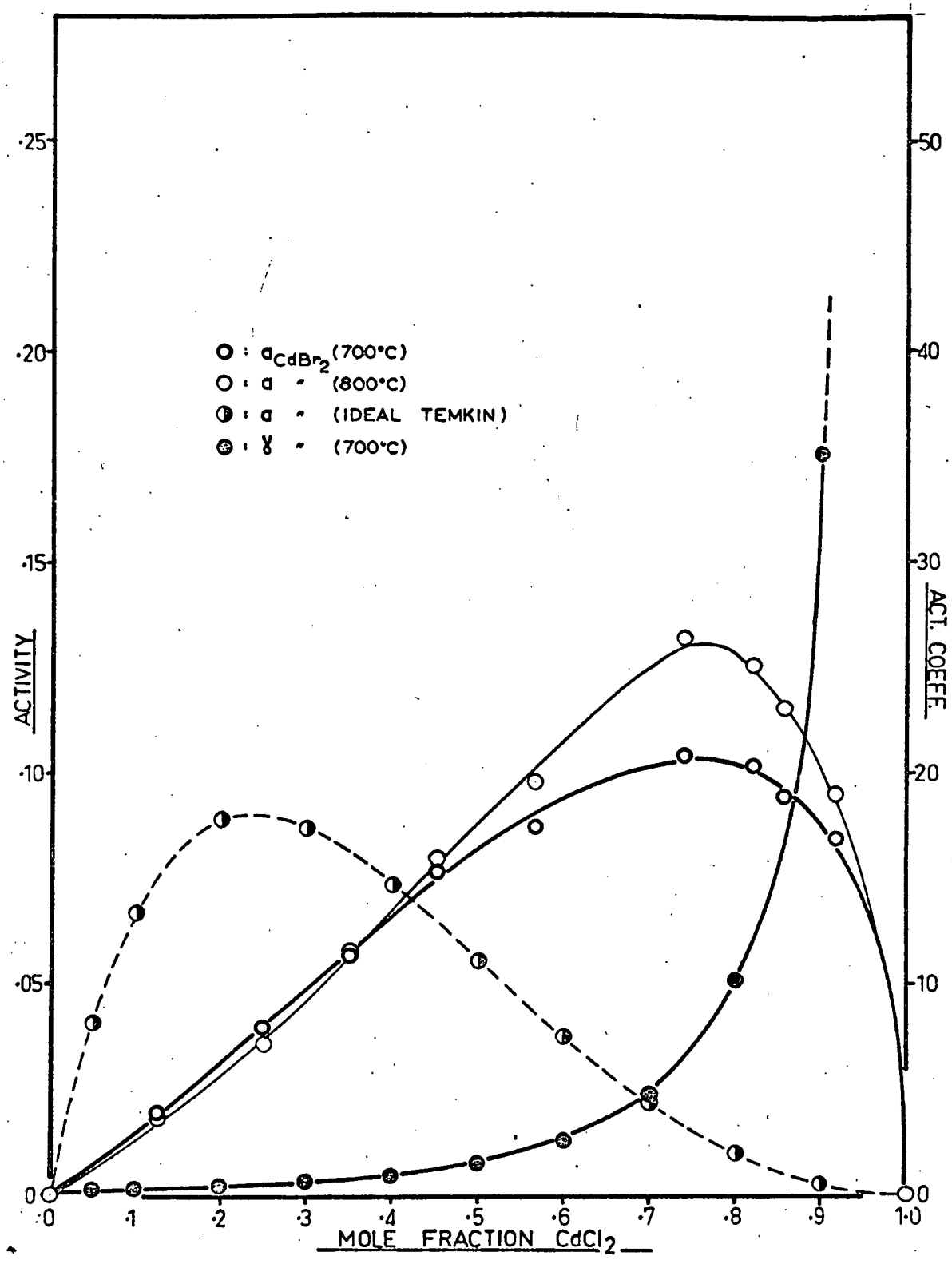



FIG. 3·63 SYSTEM $CdCl_2$–NaBr

ACTIVITY & ACTIVITY COEFF. $CdBr_2$ vs. COMPOSITION

# CHAPTER 4

# DISCUSSION OF RESULTS

## SECTION A

## THE SYSTEMS $PbBr_2$-MBr

## (M = K, Rb, Cs)

## 4A.1 INTRODUCTION

In consideration of the alkali halides, Lumsden[1], concludes that in the liquid state the local arrangement bears some resemblance to the NaCl structure. In other words, for the molten alkali halide $M^+X^-$, each anion will have as nearest neighbour, six cations situated approximately at the ends of three mutually perpendicular diameters of a sphere of radius $r_{MX}$, where $r_{MX}$ is the interionic separation of $M^+$ and $X^-$. For a molten mixture of two alkali metal halides with a common anion, i.e., $M^+X^-$ and $N^+X^-$, each cation will be surrounded by six anions on three mutually perpendicular axes, at distances $r_{MX}$ and $r_{NX}$ respectively. The immediate environment of each cation in the solution will be the same as in the pure halide melt and there will be no change of energy on mixing due to simple interaction between nearest neighbours. Lumsden regards the interactions between more distant neighbours to be of two types: (1) London forces[2] between cations, and (2) polarizing forces due to dissimilar cations in contact with the same anion.

The non-polar London forces acting between the ions give an energy term of the form:

$$E_L = C/r^6, \qquad (4.1)$$

where C is a constant. Since this function decreases rapidly with distance, the only important non-polar interactions will be between next nearest neighbours. It can be deduced[1] that the change of

---

1. Lumsden: Disc. Faraday Soc., 32 138 (1961)
2. London: Z. Physik. Chem., B11 222 (1930)

potential energy on mixing due to the London forces is:

$$E_L = K_L \, nm/(m + n) \tag{4.2}$$

$$\text{where } K_L = 6N\left[\frac{C_{MM}}{(2r^2_{MX})^3} + \frac{C_{NN}}{(2r^2_{NX})^3} - \frac{2C_{MN}}{(r^2_{MX} + r^2_{NX})^3}\right] \tag{4.3}$$

" m,n = no. of moles MX and NX respectively,

" $C_{MM}$ = interaction constant for $M^+ — M^+$ pairs, etc.,

" $r_{MX}$ = separation between $M^+$ and $X^-$ pairs, etc.,

" N = Avogadro number.

It can also be shown[1], that the polarization energy $E_p$, can be represented by:

$$E_p = K_p \, nm/(m + n) \tag{4.4}$$

$$\text{where } K_p = -1.92 \, N \alpha e^2 \left[\frac{1}{r^2_{MX}} - \frac{1}{r^2_{NX}}\right]^2 \tag{4.5}$$

" $\alpha$ = polarizability of the anion,

" e = electronic charge.

The heat of mixing of m moles of MX with n moles of NX is:

$$\triangle H = E_L + E_p$$

$$= Kmn/(m + n) \tag{4.6}$$

$$\text{where } K = K_L + K_p \tag{4.7}$$

Equation 4.7 implies that the two cations $M^+$ and $N^+$ are randomly distributed over the cation sites. This condition is not realistic because the non-polar interactions tend to cause like cations to occupy neighbouring sites, while the polarizing forces tend to cause unlike cations to occupy sites on opposite sides of the same anion. Lumsden maintains that provided the interactions are not too large, the

---

1. Lumsden: Disc. Faraday Soc., 32 138 (1961)

distribution of cations will be approximately random and the interactions will not cause any appreciable change in the vibrational entropy; in this case the entropy of mixing will be approximately ideal. Partial differentiation of eqn. 4.6 with respect to m, leads to the following expression:

$$\Delta\bar{H}_M = \frac{(\partial H)}{(\partial m)_{y,T,P}} = K\left[\frac{(m+n)n - mn}{(m+n)^2}\right]$$

$$= K\frac{n^2}{(m+n)^2}$$

$$= K N_n^2$$

Now $\Delta\bar{G}_M = \Delta\bar{H}_M - T\ \Delta\bar{S}_M$

and because $\Delta\bar{S}_M$ is considered to be ideal, then the excess functions may be represented as:

$$\Delta\bar{G}_M^E = \Delta\bar{H}_M$$

$$= K N_n^2 \qquad (4.8)$$

$$= RT \ln \gamma_m$$

where $\gamma_m$ and $\gamma_n$ refer to the activity coefficients of the components MX and NX respectively. Lumsden and others[1], have found good agreement between thermodynamic quantities calculated from experimental results and from eqn. 4.8.

This theory has been extended to multicomponent systems containing cations of different valency. Here for example, a divalent cation is regarded as replacing two monovalent ions of somewhat smaller size. Thus generally:

$$\Delta H = \sum K_{ij}\, m_i\, m_j / \sum \partial_m \qquad (4.9)$$

---

1. Hildebrand and Salstrom, and Flood et al. (see later)

where $m_i$ refers to the number of moles of cation i etc., and $\nu$, is the cationic valency. Partial differentiation of eqn. 4.9 with respect to m, leads to expressions for the excess partial molar free energies of the components, corresponding to eqn. 4.8(1).

This regular solution approach to the problem of explaining the thermodynamic properties of molten salt solutions, was originally put forward by Hildebrand and Salstrom(2). From the data on the systems AgBr + alkali metal bromides, they found the excess chemical potential of AgBr to be a linear function of $N^2_{MBr}$. They suggested that the behaviour in these systems depend upon the nature of the bond existing in AgBr on one hand and the alkali bromides on the other. By considering the potential of the lattice, the following expression was deduced for the excess chemical potential:

$$RT \ln \gamma_{AgBr} = N^2_{MBr} (2E_{12} - E_{11} - E_{22}) \qquad (4.10)$$

where $E_{11}$, $E_{22}$ and $E_{12}$ are the contribution to the lattice potentials of $Ag^+ — Ag^+$, $M^+ — M^+$ and $Ag^+ — M^+$ pairs, respectively. The constant K' ($= 2E_{12} - E_{11} - E_{22}$) in eqn. 4.10 is of the same form as K in eqn. 4.3, derived by Lumsden. The slope of the line when $\Delta \bar{G}^E_{AgBr}$ is plotted against $N^2_{MBr}$, depends upon the relative magnitude of $E_{12}$, $E_{11}$ and $E_{22}$.

Apart from mixtures of alkali halides and the AgBr-MBr systems, molten mixtures of $CaCO_3$ and alkali metal carbonates,

---

1. Lumsden: Disc. Faraday Soc., 32 138 (1961)
2. Hildebrand and Salstrom: J. Am. Chem. Soc., 54 4257 (1932)

investigated by Flood et al.,[1,2] have also been found to exhibit properties of regular solutions.

Although the thermodynamic properties of the components in the above systems can be explained by such a regular solution model, the same does not hold for the mixtures of $PbBr_2$ with alkali metal bromides, investigated by the present author. In Table 4.1 are summarized the excess partial molar free energies in each of the systems $PbBr_2$ + MBr, where M = K, Rb or Cs. The plots of $\Delta\bar{G}^E_{PbBr_2}$ versus $N^2_{MBr}$ are shown in fig. 4.1.

The marked departures from linearity of the plots of $\Delta\bar{G}^E_{PbBr_2}$ versus $N^2_{MBr}$, in the present work, can be explained by complex ion formation. These species transform the mixtures from true binary systems having a common anion (i.e. $Pb^{2+}$, $M^+$, $Br^-$), to systems containing two cations and two or more anions (i.e. $Pb^{2+}$, $M^+$, $Br^-$, $PbBr_n^{(n-2)-}$). In this case the heats of mixing of unlike anions, as well as unlike cations, should be considered. The application of regular solution theory, in addition to calculations of ionic association constants involving a number of possible complex ions, would create considerable difficulties and the actual numerical calculations would be impossible to solve. Hence, in the following discussion, the heats of mixing of like ions in solutions containing complex ions will be neglected; the solutions will be regarded as ideal solutions involving the mixing of ions, both simple and complex.

---

1. Flood, Førland and Roald: J. Am. Chem. Soc., 71 572 (1949)
2. Flood, Førland and Grjotheim: Z. anorg. u allgem. Chem:, 276 289 (1954)

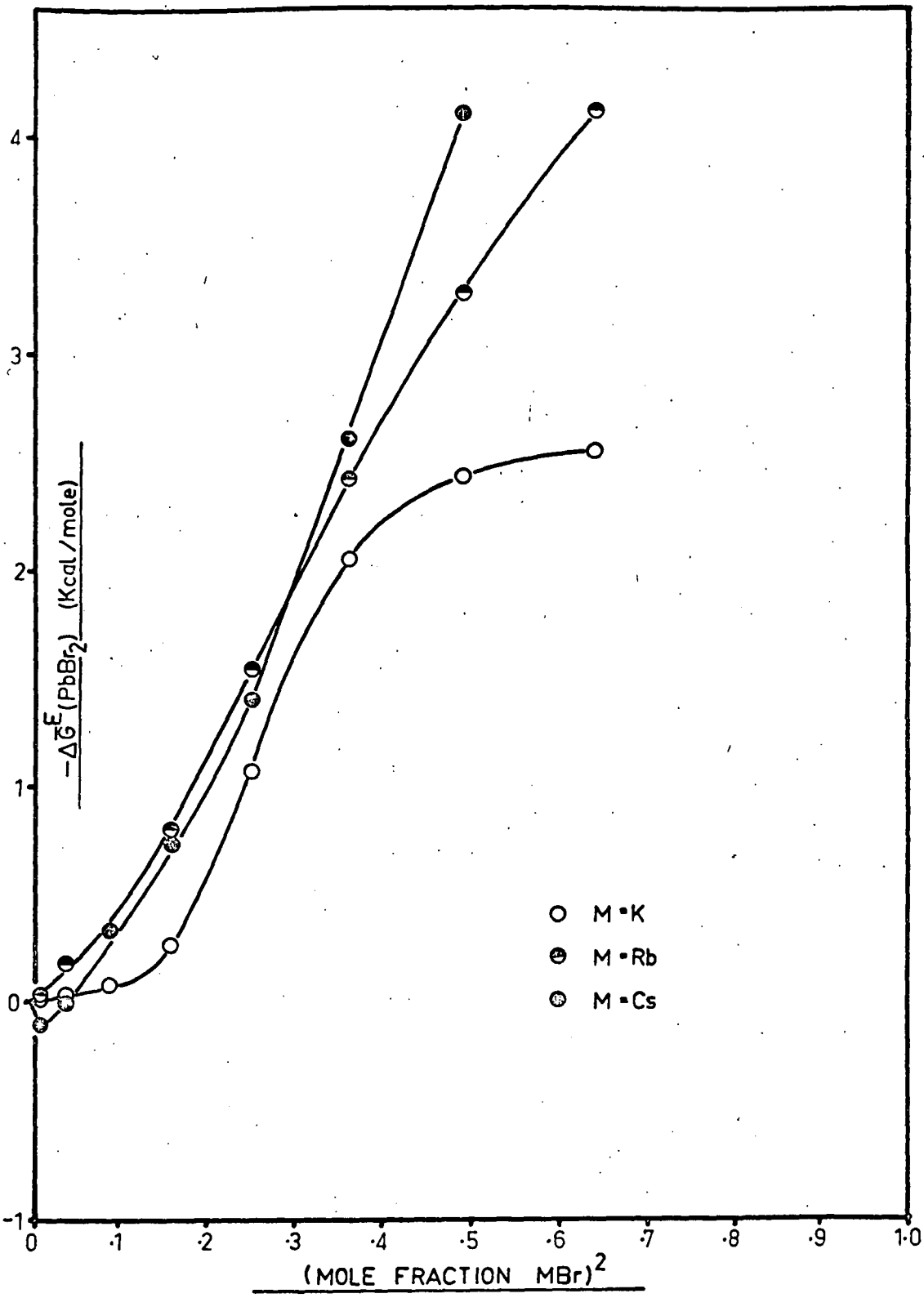



FIG. 4·1

EXCESS CHEMICAL POTENTIALS $PbBr_2$ (600°C)

SYSTEMS $PbBr_2$ — MBr

TABLE 4.1

Excess chemical potentials of $PbBr_2$ in the systems $PbBr_2$-MBr (600°C)

| $N_1$ | $N_2$ | $N_2^2$ | $-\Delta\bar{G}^E_{PbBr_2}$ (K cal/mole) | | |
|---|---|---|---|---|---|
| | | | KBr | RbBr | CsBr |
| 0.20 | 0.80 | 0.64 | 2.55 | (4.12) | - |
| 0.30 | 0.70 | 0.49 | 2.44 | 3.28 | (4.10) |
| 0.40 | 0.60 | 0.36 | 2.05 | 2.42 | 2.61 |
| 0.50 | 0.50 | 0.25 | 1.07 | 1.54 | 1.40 |
| 0.60 | 0.40 | 0.16 | 0.26 | 0.80 | 0.73 |
| 0.70 | 0.30 | 0.09 | 0.08 | 0.33 | 0.33 |
| 0.80 | 0.20 | 0.04 | 0.04 | 0.18 | 0.00 |
| 0.90 | 0.10 | 0.01 | 0.02 | 0.03 | -0.10 |

The errors involved in neglecting the heat of mixing of ions, i.e., in neglecting to treat these solutions as "regular", will affect the magnitude of calculated association constants - hence the values of association constants for complex ions, calculated in the following, are approximations obtained on the assumption that ideal mixing takes place.

## 4A.2 THERMODYNAMIC ACTIVITY OF THE COMPONENTS

a) General

In the following discussion it will be assumed that $PbBr_2$ in the standard state - the pure salt - is partially associated. In the case of lead chloride, measurements of electrical conductance indicate that the melt consists largely of ions[1]. Bloom and Heymann[2], on the basis of their measurements of the electrical conductance on the system $PbCl_2$-$CdCl_2$, have suggested either partial dissociation or auto-complexing of the lead chloride, as an explanation of the positive deviations from additivity. For very dilute solutions of $PbCl_2$ in molten $NaNO_3$, Van Artsdalen[3] has evaluated a dissociation constant for the lead halide. However, conclusions regarding the presence of undissociated species at higher concentrations cannot necessarily be considered valid. It will be assumed that lead chloride consists mainly of dissociated $Pb^{2+}$ and $Cl^-$ ions in equilibrium with undissociated molecules (or alternatively associated groups of ions) and that the same arguments apply equally to lead bromide.

(i) Positive deviations from the Temkin activity

Because of the associative tendencies of pure lead bromide, it will be assumed that a certain degree of overlap between the ion

---

1. Richards: Ph.D. thesis, University of New Zealand (1956)
2. Bloom and Heymann: Proc. Roy. Soc., A188 392 (1947)
3. Van Artsdalen: J. Phys. Chem., 60 172 (1956)

clouds of $Br^-$ and $Pb^{2+}$ occurs. As the lead ion has two outer 6s electrons, it is considered that the interaction between bromide and lead ions takes the form of a "bond" which possesses a certain degree of co-valent character. In an idealised system in which no complex ions are formed, the introduction of alkali metal ions will have the effect of polarizing the Pb — Br bond and thereby decreasing the interaction between lead and halide ions. Thus there will be an increase in the number of dissociated $Pb^{2+}$ and $Br^-$ ions above that present in the standard state, thus increasing the activity coefficient of lead bromide. Even though $Li^+$ is the only alkali metal ion with greater polarizing power than $Pb^{2+}$ (polarising power being assumed to be proportional to the surface charge density - see Table 4.2), the effect will be in the same direction with all alkali

TABLE 4.2

Charge densities for the ions of lead and the alkali metals

| metal ion | radius[1] (Å) | surface area $(Å)^2$ | charge density (e.s.u./$Å^2$) |
|---|---|---|---|
| $Pb^{2+}$ | 1.21 | 18.4 | 0.109 |
| $Li^+$ | 0.60 | 4.5 | 0.222 |
| $Na^+$ | 0.95 | 11.3 | 0.088 |
| $K^+$ | 1.33 | 22.2 | 0.045 |
| $Rb^+$ | 1.48 | 27.5 | 0.036 |
| $Cs^+$ | 1.69 | 35.9 | 0.028 |

1. Pauling: Nature of the Chemical bond: Cornell Univ. Press (1948)

ions, although the tendency will diminish through the series $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$. The positive deviations of the actual activity values from those of the ideal Temkin values (see Section 1.5b) will, for an idealised system, be greatest for $Li^+$ and smallest for the $Cs^+$ ion which has smaller polarizing power. In the system $PbCl_2$-NaCl, where complex ion formation takes place only to a very limited extent (if at all), the positive deviations of $a_{PbCl_2}$ can be explained in the above terms.

(ii) Negative deviations from the Temkin activity

Case I: Alkali metal ions of low polarizing power.

The addition of such alkali metal halides as RbBr to pure lead bromide will cause a dilution effect resulting in a greater separation between nearest neighbour $Pb^{2+}$ ions. The interactions between these will therefore occur to a lesser extent than in pure $PbBr_2$. Consequently, the tendency will be for the bromide ion atmospheres to be deformed towards the more polarizing $Pb^{2+}$ ion. This can have one of two consequences: (1) increased interaction between the $Pb^{2+}$ and $Br^-$ ions of lead bromide, or (2) provided sufficient orbital overlap is established, co-valent species, containing lead ions and more than twice the number of halide ions, can be formed, for example, associations such as $PbBr_3^-$, $PbBr_4^{2-}$ and $PbBr_6^{4-}$. (Throughout the following discussion these entities will be referred to as complex ions.) Both these tendencies will have the effect of removing "free" $Pb^{2+}$ and $Br^-$ ions from the melt and so lower the activity of lead bromide. The following discussion is based on the second alternative.

Consider the formation of the complex ion $PbBr_3^-$ after the addition of a small amount of MBr (for example, a mixture containing 80 mole % $PbBr_2$ and 20 mole % MBr). Then, if quantitative formation is assumed, such an entity will be present in the proportion $PbBr2 : PbBr_3^- = 1 : 3$. This species, however, will still be subjected to the polarizing forces of the remaining $Pb^{2+}$ ions, so that no one $Pb^{2+}$ ion will remain associated with the same three $Br^-$ ions, but rather an equilibrium between all the lead and bromide ions will result. Similar equilibria can be proposed for species having more than one extra halide ion in equilibrium, such as $PbBr_4^{2-}$ etc. At the composition corresponding to the stoichiometry of a complex ion, the only "free" lead and bromide ions in the melt will be those due to the dissociation of that species, (provided that this is the only complex ion present and provided that all the $PbBr_2$ and MBr go to form the appropriate complex).

Investigations of molten salt systems suggest that in many cases, complex ions of more than one type exist in equilibrium. For the moment it will be assumed that in the system $AX_2$-MX, the only ions present in an equimolar mixture are $A^{2+}$, $X^-$, $M^+$ and $AX_3^-$. Additions of further alkali halide to the mixture will have one of two effects: (1) increase in the number of "free" $X^-$ ions and at the same time, increased polarization of the A — X bond as a result of the intensification of the electrostatic field (due to more $M^+$ ions), or (2) deformation of further halide ionic atmospheres, leading to the formation of species containing a greater ratio of $X^-$ to $A^{2+}$. Effect (1) will result in an increased activity of $AX_2$ due to the dissociation

of $AX_3^-$, whereas (2) will result in a decreased activity. The measured activity coefficients can be used to decide between the alternatives. If $\gamma AX_2$ exhibits a continued decrease below the value at 0.5 mole fraction $AX_2$, then it is probable that the number of dissociated $A^{2+}$ and $X^-$ ions has decreased from that present in the equimolar mixture. Provided that the activity coefficient still shows the same tendency when the mole ratio of $AX_2$ : MX = 1:2, then either the $AX_3^-$ species has associated with a further halide ion, or the trihalide species does not exist in this composition region and the decrease in $\gamma AX_2$ up to 0.33 mole fraction $AX_2$, is due solely to an increase in the concentration of $AX_4^{2-}$. Similarly, if $\gamma AX_2$ continues to show a decreased value below 0.33 mole fraction $AX_2$, it is indicative that species having more than $4X^-$ ions per $A^{2+}$ ion are predominent, e.g., $AX_6^{4-}$.

In each case, the decrease in the activity coefficient with increasing concentrations of MX, is associated with an increase in the co-valent character of the bonding between separate ions in the melt. From considerations of the packing of ions, it is unlikely that the number of halide ions associated with each lead ion exceed six. Hence, further additions of alkali halide to mixtures containing 20 mole% $AX_2$ in which the six co-ordinated ion is present, can result only in a decreased association between $A^{2+}$ and $X^-$ ions, with the result that the activity coefficient will show a minimum value at this composition. However, for the case where an ion such as $AX_6^{4-}$ is sufficiently stable to be unaffected by polarizing influences, then further additions

of MX to mixtures containing 80 mole%, will have no effect on the dissociation of the complex. The activity coefficient of $AX_2$ will therefore tend to a constant value and exhibit no minimum.

On the basis of the preceding considerations, the following dissociation scheme may be formulated, involving the three complex ions $AX_3^-$, $AX_4^{2-}$ and $AX_6^{4-}$:

$$A^{2+} + 3X^- \overset{K_1}{\rightleftharpoons} AX_3^-$$

$$A^{2+} + 4X^- \overset{K_2}{\rightleftharpoons} AX_4^{2-}$$

$$A^{2+} + 6X^- \overset{K_3}{\rightleftharpoons} AX_6^{4-}$$

$$\text{or } A^{2+} + 3X^- \rightleftharpoons AX_3^- \rightleftharpoons AX_4^{2-} \rightleftharpoons AX_6^{4-}$$

$$+ X^- \qquad + 2X^-$$

where $K_1$, $K_2$ and $K_3$ are the association constants of the three species.

A less conventional scheme may also be proposed involving large ionic species such as $A_4X_9^-$, by analogy with known inorganic compounds[1-3], though the presence of such species in molten salts has yet to be confirmed at temperatures other than those near the melting points of the mixtures. It is considered possible that species such as $A_4X_9^-$ may be formed in mixtures rich in $AX_2$, e.g., 80 mole % $AX_2$. Subsequent additions of alkali halide would cause dissociation into species containing a higher proportion of halide ions per lead ion. Such a scheme may be represented as follows:

$$A_4X_9^- \rightleftharpoons 2A_2X_5^- \rightleftharpoons 4AX_3^- \rightleftharpoons 4AX_4^{2-} \text{ ... etc.}$$

$$+ X^- \qquad + 2X^- \qquad + 4X^-$$

---

1. Powell and Tasker: J. Chem. Soc., 119 (1937)
2. Hastie: B.Sc.(hons.) thesis, University of Tasmania (1964)
3. Easteal: Ph.D. thesis, University of Tasmania (1964)

Lantratov and Shevlyakova[1], in their measurements of the activity of lead bromide, have proposed the presence of the complex ion $Pb_2Br_5^-$, in the system $PbBr_2$ - KBr. However, more evidence is needed to confirm (or deny) this proposition.

Case II: Alkali metal ions of high polarizing power.

Strongly polarizing cations ($M^+$), will tend to polarize co-valent "bonds" of complex species, so that the bonds will acquire a higher degree of ionic character. The stability of the complexes will therefore be greatly reduced and in most cases the complex ions are regarded as being largely dissociated. The resulting decrease in the equilibrium concentration of these species, will result in a more ideal activity, compared to case I.

Thus the addition of MBr to $PbBr_2$ will theoretically present two opposing effects: on one hand, dissociation of lead bromide into the simple ions $Pb^{2+}$ and $Br^-$, thereby resulting in an increase in the activity of $PbBr_2$; on the other hand, the formation of associated species which remove "free" $Pb^{2+}$ and $Br^-$ ions from the melt and contribute to a decrease in $a_{PbBr_2}$. The observed activity will therefore depend upon the stability of the complex and the polarizing field of the alkali metal cation to which it is subjected. In the case of $Li^+$, the first tendency may be regarded as the only one in operation, so that over the whole composition range a positive deviation from the ideal activity will be observed. This is the case for the

---

1. Lantratov and Shevlyakova: Russ. J. Inorg. Chem., 4 523 (1959)

system $PbCl_2$ - LiCl[1,2]. The sodium ion on the other hand, with a charge density 2½ times less than that of $Li^+$ will, because of its lower polarizing power, tend to permit to a certain extent, the formation of complexes, so that less positive or small negative deviations in the activity will result. The magnitude of the negative deviation will depend on the stability of the complexes and hence on the alkali halide component present. The deviations from Temkin activity values will become more negative as the polarizing power of the alkali metal cation decreases.

Theoretically, if a complex ion has an infinite stability constant, then effectively all but the alkali metal ions are bound within the species, thereby reducing the activity of each component to zero*. Thus in the system $AX_2$ - MX, at the composition 1/(z-1) mole fraction $AX_2$, corresponding to the stoichiometric composition of the complex ion $AX_z^{(z-2)-}$, the activity of either $AX_2$ or MX can vary between 0 to 1/(z-1) and 0 to (z-2)/(z-1) respectively, depending on whether the melt is completely associated into $AX_z^{(z-2)-}$ and $M^+$, or completely dissociated into the independent simple ions. Theoretically, the maximum deviation possible for $a_{MX_2}$ and $a_{AX}$, assuming the complex ion $AX_z^{(z-2)-}$, will therefore be 1/(z-1) and (z-2)/(z-1) respectively.

---

1. Lantratov and Alabyshev: Zhur. Priklad. Khim., 26 263 (1953)
2. Markov, Delimarskii and Panchenko: Zhur. Fiz. Khim., 29 51 (1955)

*. This is only true if no excess of either component is present.

In the view of the present author, many activity results have been wrongly interpreted. Consider the case where z = 3. Suppose in the system $AX_2$ - MX, that the activity versus composition isotherm for $AX_2$, deviates from the Temkin activity by 0.25 units at 50 mole % $AX_2$ and 0.20 units at 20 mole % $AX_2$ (0.20 units deviation for $AX_2$ for the composition 20 mole % $AX_2$ is the maximum possible value, i.e., $a_{AX_2} = 0$, and therefore no "free" ions of $A^{2+}$ and $X^-$ can be present). The maximum deviation of $a_{AX_2}$ for the equimolar mixture of $AX_2$ + MX has been attributed to the presence of the complex ion $AX_3^-$ even though the entity $AX_6^{4-}$ may be completely undissociated. Therefore the fact that a maximum deviation from the Temkin activity occurs at a certain mole fraction, does not necessarily mean that the greatest interaction takes place at that composition.

The only criterion for estimating the greatest interaction (greatest co-valent character of the bonding between ions) within the melt, is by the minimum value of the activity coefficient, which has already been mentioned. Unfortunately, few mixtures have been investigated above about 80 mole % alkali halide, so that the position of the minimum in many cases cannot be ascertained. An alternative procedure is to compare the percentage deviation ( $\Delta$a%), from the ideal activity at different compositions, i.e. ( $\Delta$a exptl./ $\Delta$a max.) x 100, where $\Delta$ a exptl., is the deviation of the experimental from the Temkin activity and $\Delta$ a max., the excess of the Temkin activity above zero at the same composition. This however does not give a precise comparison because the deviation is not directly proportional to the degree of dissociation.

(iii) The effect of temperature on the thermodynamic activity

1) As the temperature is raised, the increase in the thermal vibration of the ions in the melt will cause the degree of dissociation of co-valently bound species and ion pairs to increase. The increased number of "free" ions will thereby result in an activity closer to the ideal.

2) A change in temperature will have a slight effect on the heat of mixing. If the mixture, in the first instance, is regarded as approximating to an ideal solution, then the heat of mixing, $\Delta H$ mix., will be given by[1]:

$$\Delta H \text{ mix.} = N_1 N_2 \lambda \left(1 - N_1 N_2 \frac{2\lambda}{Z' RT}\right) \qquad (4.11)$$

where $N_1$ and $N_2$ = mole fraction of components 1 and 2

$\lambda$ = $(2E_{12} - E_{11} - E_{22})$ - see Section 4A.1

$Z'$ = no. of cation nearest neighbours of each cation

$R$ = gas constant

$T$ = absolute temperature

If the system $PbCl_2$-KCl, investigated by Lantratov and Alabyshev[2], is used as an example, then: $Z' = 12$; $\lambda = -5700$ cal/mole (assumed to be independent of temperature); $N_1 = 0.4$; $N_2 = 0.6$; $R = 1.987$ cal/deg/mole.

For $T = 1000^{\circ}K$, $\Delta H$ mix. = -1524 cal/mole.

For $T = 1100^{\circ}K$, $\Delta H$ mix. = -1510 cal/mole.

---

1. Blander: Molten Salt Chemistry, Interscience (1964)

2. Lantratov and Alabyshev: Zhur. Priklad. Khim., 26 263 (1953)

Thus, a temperature increase of 100°C, changes the heat of mixing by 14 cal/mole in the direction of a more ideal solution. This is such an insignificant change that the effect on the activity of the components will be negligible. Because it is found experimentally that activity results show considerable changes with temperature, such solutions can neither be regarded as ideal, nor regular.

3) When the (ionic) crystals and the vapours of alkali halides are compared, a decrease in the interionic distance is observed on vaporization. This is correlated with a distruction of the symmetrical electrostatic forces in the ordered solid acting on any particular ion. As a result, the attractive forces between oppositely charged ions are increased. The vapours of the alkali halides in fact,are regarded as consisting largely of co-valently bound ion pairs, e.g., NaCl (these may also be associated into dimers, e.g. $(NaCl)_2$ and trimers, e.g. $(NaCl)_3$ etc.) The melt, lying between the extremes of solid and vapour, is also accredited with a more co-valent nature of the "bonding" between ions relative to the crystalline state, because the randomisation of the constituent species increases the asymmetry of the electrostatic forces.

An increase in temperature of the melt, will cause a more random distribution of species, with an increase in the asymmetry of the force fields due to the increase in molar volume. If in the system $PbBr_2$-MBr, the melt is regarded as consisting of the ions:

$Pb^{2+}$, $Br^-$, $M^+$, $PbBr_n^{(n-2)-}$, then as the temperature is raised, so will there be an increased tendency for oppositely charged ions to associate. Such associations may be represented as follows:

| | |
|---|---|
| $Pb^{2+}.\ 2Br^-$<br>$Pb^{2+}.\ Br^-$ | these effects will also occur in the standard state |
| $M^+.\ Br^-$<br>$M^+.\ PbBr_n^{(n-2)-}$<br>$Pb^{2+}.\ PbBr_n^{(n-2)-}$ | these effects will occur in addition to those in the standard state |

The overall tendency with increase of temperature, will therefore be for the number of "free" ions to be decreased and thus result in a decrease in the activity of the component salts. This effect is in opposition to effect (1).

The two most predominant effects with increase in temperature are considered to be increased dissociation of co-valently bound ions and increased association as ion pairs. The nature of the interaction between $Pb^{2+}$ and $X^-$ and the environmental influence of the alkali metal ion present will determine the dominant effect. It is the opinion of the author, that the stronger the $Pb^{2+}$— $X^-$ "bond", the less will be the thermal dissociation with increase of temperature. In such a case, the relative increase in the numbers of co-valently bound ion pairs will exceed the "free" $Pb^{2+}$ and $Br^-$ ions caused by dissociation of complex ions on heating and a decrease in the activity of the component salts will thus result.

b) The system $PbBr_2$-KBr

The activity and activity coefficient of $PbBr_2$ show small negative deviations from ideal values in the composition region 0.6-1.0 mole fraction $PbBr_2$ (see fig. 3.4, Table 4.3). The magnitude of the activity deviation in this range of composition is

TABLE 4.3

Percentage deviation of the activity of $PbBr_2$ from the Temkin activity, in the system $PbBr_2$-KBr (600°C)

| m.f. $PbBr_2$ | .20 | .25 | .30 | .35 | .40 | .45 | .50 | .55 |
|---|---|---|---|---|---|---|---|---|
| $-\Delta a_{PbBr_2}$ (%) | 80 | 80 | 77 | 74 | 70 | 62 | 46 | 24 |
| m.f. $PbBr_2$ | .60 | .65 | .70 | .75 | .80 | .85 | .90 | .95 |
| $-\Delta a_{PbBr_2}$ (%) | 14 | 9 | 6 | 5 | 4 | 3 | 2 | 1 |

very similar to that for the system $PbBr_2$-NaBr which was investigated by Lantratov and Shevlyakova[1]. As the proportion of KBr increases from 40 to 60 mole %, the activity and activity coefficient of $PbBr_2$ decrease at a much greater rate. This is attributed to interactions within the melt resulting in the formation of associated species. For mixtures richer (in KBr) than 40 mole %, the rate of decrease of the activity coefficient with composition becomes progressively smaller, until in the region of 0.2-0.3 mole fraction $PbBr_2$ where it is approximately constant. The calculated activity for the composition 0.197 mole fraction $PbBr_2$ is not sufficiently accurate to ascertain whether the activity coefficient does in fact reach a minimum value in

1. Lantratov and Shevlyakova: Russ. J. Inorg. Chem., 4 523 (1959)

such mixtures or not. It appears that complex ion formation plays a minor role in the range 1.0-0.6 mole fraction $PbBr_2$. The greater rate of change of the activity coefficient with composition thereafter, can be explained either in terms of the formation of the complex ion $PbBr_4^{2-}$ or an equilibrium between $PbBr_3^-$ and $PbBr_4^{2-}$, i.e.,

$$Pb^{2+}.\ 2Br^- + Br^- \rightleftharpoons PbBr_3^- \rightleftharpoons PbBr_4^{2-}$$
$$+\ Br^-$$

The presence of the tribromide anion alone is insufficient to account for the still rapid deviation of $\gamma_{PbBr_2}$ and $\Delta a_{PbBr_2}$ in mixtures richer than 50 mole % KBr. The stoichiometry of the species $PbBr_4^{2-}$ corresponds to the composition 0.33 mole fraction $PbBr_2$ and because of the pronounced decrease in gradient of the activity coefficient versus composition curve (and also the much smaller increments in $\Delta a_{PbBr_2}$) with further additions of KBr, it is considered that the four co-ordinated ion is the most stable in these solutions. The ion $PbBr_6^{4-}$, if present, is only a minor constituent because there is a negligible decrease in $\gamma_{PbBr_2}$ between 0 and 0.30 mole fraction $PbBr_2$.

This work is not in quantitative agreement with that of Lantratov and Shevlyakova[1], where much larger activity deviations are recorded at corresponding temperatures and compositions. However, the accuracy of their work is somewhat questionable in the light of their measured values for $E^\circ$ at various temperatures (see fig. 3.1). By analogy with the two incongruently melting compounds, $2PbBr_2.KBr$ and $PbBr_2.2KBr$, from the phase diagram, Lantratov and Shevlyakova state that the complexes present are $Pb_2Br_5^-$ and $PbBr_4^{2-}$, a deduction which

---

1. Lantratov and Shevlyakova: Russ. J. Inorg. Chem., 4 523 (1959)

is plausible but not necessarily correct. In this work, the fact that at 0.667 mole fraction $PbBr_2$, the deviation of the activity of $PbBr_2$ from the ideal value is of the order of 7% (compared to $\Delta a_{PbBr_2} = 88\%$ at 0.25 mole fraction $PbBr_2$), suggests that $Pb_2Br_5^-$ is not a predominant species.

Over almost the whole composition range, the activity of $PbBr_2$ shows an increase with increase of temperature. In the composition range 0.45-0.60 mole fraction $PbBr_2$, an increase of 0.06 units is observed for a 100°C temperature rise, a difference which gradually diminishes as the mixture becomes richer or poorer in $PbBr_2$. This trend is consistent with the view that polarization by potassium ions weaken the Pb — Br "bonds" sufficiently to allow increased thermal vibration to predominate over the tendency for increased ion pair formation with increase of temperature. In the vicinity of the 20 mole % $PbBr_2$ composition, the reverse effect is observed. The interpretation of this phenomenon is dubious however, owing to the uncertainty in the measured activity at this composition.

c) <u>The system $PbBr_2$-RbBr</u>

From the initial addition of RbBr to $PbBr_2$, the activity and activity coefficient of $PbBr_2$ show a steadily increasing deviation until the 45 mole % $PbBr_2$ composition (see fig. 3.10, Table 4.4). The activity then tends to zero (with correspondingly lower values than for the previous system) as the mole fraction of RbBr tends to unity.

TABLE 4.4

Percentage deviation of the activity of $PbBr_2$ from the Temkin activity in the system $PbBr_2$-RbBr (600°C)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| m.f. $PbBr_2$ | .20 | .25 | .30 | .35 | .40 | .45 | .50 | .55 |
| $-\Delta a_{PbBr_2}$ (%) | 90 | 88 | 87 | 80 | 75 | 69 | 59 | 48 |
| m.f. $PbBr_2$ | .60 | .65 | .70 | .75 | .80 | .85 | .90 | .95 |
| $-\Delta a_{PbBr_2}$ (%) | 33 | 25 | 17 | 11 | 6 | 2 | 1 | - |

Over the composition range studied, there is no tendency for the activity coefficient to show a minimum value, although the percentage deviation of the activity of $PbBr_2$ (obtained by extrapolation) from the ideal curve, shows a less rapid increase between 70 and 80 mole % RbBr. Although the activity coefficient of $PbBr_2$ shows a more gradual change as the concentration of alkali halide increases from 0-0.25 mole fraction MBr in comparison with more dilute $PbBr_2$ solutions, it still indicates a greater interaction between $Pb^{2+}$ and $Br^-$ in this region than for the system $PbBr_2$-KBr. It is assumed therefore, that covalently bound complex ions are formed with the initial additions of rubidium bromide. This, in the first instance, would be due to the 1.25 times lower polarization of the Pb — Br bond by the $Rb^+$ ion in comparison to the $K^+$ ion. The continued rate of decrease of the activity coefficient with composition for mixtures containing less than 33 mole % $PbBr_2$, indicates that the strongest interactions occur for mole fractions of lead bromide of 0.2 or greater. This is also suggested by the percentage deviation of $a_{PbBr_2}$. Thus, it seems reasonable to assume that the most stable ion in molten $PbBr_2$-RbBr

solutions is $PbBr_6^{4-}$.

For mixtures containing more than 45-50 mole % RbBr, the rate of decrease of $\gamma_{PbBr_2}$ with composition is smaller with respect to mixtures containing less than 45 mole % RbBr. This is indicative of the presence of complex ions with smaller ratios of $Br^-:Pb^{2+}$. The absence of these would result in a more uniform decrease in $\gamma_{PbBr_2}$ up to 80 mole % RbBr. Therefore, for this system, the following ions are assumed to be in equilibrium:

$$Pb^{2+} + 2Br^- \overset{K_1}{\rightleftharpoons} PbBr_3^- \overset{K_2}{\rightleftharpoons} PbBr_4^{2-} \overset{K_3}{\rightleftharpoons} PbBr_6^{4-}$$

$$+ Br^- \quad + Br^- \quad + 2Br^-$$

where $K_1$, $K_2$ and $K_3$ are the association constants for the species $PbBr_3^-$, $PbBr_4^{2-}$ abd $PbBr_6^{4-}$, respectively and $K_3 > K_2 > K_1$.

With increasing temperature the activity of $PbBr_2$ shows an increase over the whole composition range. This increase is, however, much smaller in magnitude than in the system $PbBr_2$-KBr (0.01-0.02 mole fraction units). Although the rubidium ion will polarize the Pb — Br "bond" less than the potassium ion, it still weakens the bonds of the complex ions sufficiently, to allow the increased dissociation of complex species due to increased temperature to be the more dominant effect.

d) <u>The system $PbBr_2$-CsBr</u>

For mixtures containing up to 43 mole % $PbBr_2$, the values of the activity of lead bromide in this system, although lower by approximately 0.01 units, are very similar in magnitude to those for the system $PbBr_2$-RbBr (see fig. 3.16, Table 4.5). The decreased

TABLE 4.5

Percentage deviation of the activity of $PbBr_2$ from the Temkin activity in the system $PbBr_2$-CsBr (600°C)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| m.f. $PbBr_2$ | .20 | .25 | .30 | .35 | .40 | .45 | .50 | .55 |
| $-\Delta a_{PbBr_2}$ (%) | 95 | 92 | 90 | 86 | 79 | 67 | 54 | 45 |
| m.f. $PbBr_2$ | .60 | .65 | .70 | .75 | .80 | .85 | .90 | .95 |
| $-\Delta a_{PbBr_2}$ (%) | 35 | 26 | 18 | 8 | 1 | -4 | -6 | - |

activity is to be expected because of the lower polarizing power of the alkali metal ion and the resulting increased stability of the co-valent complexes. For compositions between 43 and 70 mole % $PbBr_2$, activities of $PbBr_2$ in both the $PbBr_2$-RbBr and $PbBr_2$-CsBr systems are very similar, while for mixtures containing more than 75 mole % $PbBr_2$ the systems differ appreciably. The positive deviation in the activity of lead bromide in mixtures with CsBr (for compositions rich in $PbBr_2$), is contrary to the tendency expected. The cesium ion has a lower charge density than the rubidium ion and would have been expected, therefore, to polarize any co-valent complex species to a lesser degree, thereby contributing to a lower activity of $PbBr_2$. There are two possible explanations for this behaviour: (1) The activity of $PbBr_2$ is in agreement with that predicted by Hildebrand for the complex species $PbBr_4^{2-}$ (see Section 4A.6a(ii));

(2) Consider the proposition, that interactions between $Pb^{2+}$ and $Br^-$ in concentrated solutions of $PbBr_2$ with alkali metal bromides lead to the formation of large ionic aggregates such as $Pb_4Br_9^-$. It would then be possible for the large size of the cesium ion to prevent the

packing of simple ions into these large clusters. Not until higher concentrations of CsBr, when the formation of smaller complex ions is favoured, will this effect be overcome. In the composition range 80-100 mole % $PbBr_2$, the only effect of the $Cs^+$ ion will therefore be the polarization of the Pb — Br "bonds" of the undissociated lead bromide, resulting in an increase in the number of "free" $Pb^{2+}$ and $Br^-$ ions. Thus the resultant effect will be for an increase in the activity of $PbBr_2$ above the ideal value.

Arguments against this latter postulate are:

(1) Positive deviations of $a_{PbBr_2}$ from the Temkin activity, are larger than expected for the low polarizing $Cs^+$ ion.

(2) The increase in excess free volume (see Section 4A.5) would be thought to allow the orientation of large complex ions in spite of the size of the $Cs^+$ ion.

(3) The presence of ions such as $Pb_4Br_9^-$ in the melt is unlikely. However, apart from the two suggestions for the positive deviation in $a_{PbBr_2}$ no others are at present apparent.

Over the composition range studied, no minimum in the activity coefficient for lead bromide is observed, although between 20 and 30 mole % $PbBr_2$, $\Delta a_{PbBr_2}$ tends to become constant. It is concluded therefore, that as in the previous system, the predominent complex ion is $PbBr_6^{4-}$. Also the more uniform decrease in $\gamma_{PbBr_2}$ from 20-65 mole % CsBr, compared with the system $PbBr_2$-RbBr, suggests that species such as $PbBr_3^-$ and $PbBr_4^{2-}$ are not so predominent as in the other systems.

The charge density of the cesium ion is approximately 30% less than for the rubidium ion. The stability of complex ions in the system $PbBr_2$-CsBr will therefore be noticeably greater than for the system $PbBr_2$-RbBr, so that less "free" ions will be produced due to thermal dissociation in the former system. The most predominant effect of an increase in temperature may therefore be an increase in ion pair formation, resulting in an overall decrease in the activity of $PbBr_2$. This is observed experimentally for mixtures containing 45-100 mole % $PbBr_2$ (+ 0-55 mole % CsBr). Below this composition, a very small increase in activity per 100°C rise in temperature is noted but this is of the same order as the experimental error.

Throughout the series of alkali bromides, KBr, RbBr, CsBr, in the systems $PbBr_2$-MBr, the tendency is for an increase in the deviation of both $a_{PbBr_2}$ and $a_{MBr}$ from the ideal Temkin values due to an increase in the stability of the complex ions. This is attributed to a decrease in the polarization of the Pb — Br "bonds" of the complex species by the $M^+$ ions. The species $PbBr_6^{4-}$ is regarded as being the most stable in the systems $PbBr_2$-RbBr and $PbBr_2$-CsBr, for mixtures rich in MBr, with the ions $PbBr_4^{2-}$ and $PbBr_3^-$ being of lesser importance as the size of the alkali metal ion increases. In the system $PbBr_2$-KBr the most important complex species is regarded as being $PbBr_4^{2-}$.

Support for the proposition that the degree of co-valent character of the bonding in the complex ions varies inversely with the

polarization by the alkali metal ions, comes from the activity versus temperature relationships. The decreasing dissociation of complex ions as the temperature is increased through the series $PbBr_2$-KBr, $PbBr_2$-RbBr, $PbBr_2$-CsBr, is apparent, since the more dominant tendency is ion association.

## 4A.3 FREE ENERGIES

The variation of the partial molar free energies of $PbBr_2$ with composition, for mixtures with KBr, RbBr and CsBr, are shown in figs. 3.5, 3.11 and 3.17 respectively, as are the corresponding partial free energies for the alkali halide component. These show the same deviations as the activities of the salts in these binary mixtures and because of the relationship between them, (eqn. 1.61), can be interpreted in the same manner. Excess partial molar functions for $PbBr_2$ are represented in the same figures and these are directly correlated to the deviations of the experimental activity from the ideal Temkin activity. The tendency for the excess chemical potential to become more negative in each case, represents the energy evolved as a result of complex formation. The excess positive value in the case of the system $PbBr_2$-CsBr, in the region 80-100 mole % $PbBr_2$, is indicative of energy expended in the breakdown of associated $PbBr_2$ molecules, as suggested by the activity results.

The integral free energies of mixing ($PbBr_2$ with MBr), are shown in figs. 3.5, 3.11 and 3.17 and the excess free energies are presented in Table 4.6. The latter have been calculated from the relationship:

$$\Delta G^E = \Delta G - \Delta G^i \qquad (4.12)$$

where $\Delta G^i$ = ideal free energy of mixing

$$= N_1 \Delta \bar{G}_1^i + N_2 \Delta \bar{G}_2^i \qquad (4.13)$$

$$\text{where } \Delta\bar{G}_1^{\,i} = \text{ideal partial molar free energy of component 1} = RT \ln N_1$$
$$\text{"} \quad \Delta\bar{G}_2^{\,i} = RT \ln N_2 \qquad (4.14)$$

TABLE 4.6

Excess free energies ; in the system $PbBr_2$-MBr (600°)

| $N_1$ | $N_2$ | $-\Delta G^E$ (K cal/mole) | | | |
|---|---|---|---|---|---|
| | | ideal | KBr | RbBr | CsBr |
| 0.10 | 0.90 | 0.566 | 0.89 | 1.52 | 1.75 |
| 0.20 | 0.80 | 0.870 | 1.23 | 2.03 | 2.67 |
| 0.30 | 0.70 | 1.063 | 1.42 | 2.26 | 3.13 |
| 0.40 | 0.60 | 1.171 | 1.56 | 2.34 | 3.11 |
| 0.50 | 0.50 | 1.205 | 1.55 | 2.28 | 2.91 |
| 0.60 | 0.40 | 1.171 | 1.37 | 2.05 | 2.53 |
| 0.70 | 0.30 | 1.063 | 1.11 | 1.70 | 2.03 |
| 0.80 | 0.20 | 0.870 | 0.76 | 1.19 | 1.41 |
| 0.90 | 0.10 | 0.566 | 0.35 | 0.61 | 0.65 |
| Position of maximum (mole fraction $PbBr_2$) | | 0.52 (NaBr) | 0.45 | 0.40 | 0.34 |
| Maximum deviation* (-K cal/mole) | | 0.48 (NaBr) | 1.57 | 2.34 | 3.14 |

* estimated values

Because $\Delta G$ is a measure of the energy evolved on mixing the two components $PbBr_2$ and MBr (i.e. the spontaneity of the process), it is evident that the stabilities of the associated groups formed, increase from $K^+$ to $Cs^+$ over the entire composition range. This supports the deduction from the activity results, that ions of low polarizing power

have a lesser effect on the dissociation of complex species than highly polarising ions.

It is interesting to note the shift in the position of the maximum for the excess integral free energy towards mixtures richer in the alkali halide component, as the radius of the alkali metal ion is increased. The value of $\Delta G^E$ for the system $PbBr_2$-NaBr, has been obtained from the work of Lantratov and Shevlyakova[1]. The position and magnitude of the maxima are compared in Table 4.6. This indicates that as the polarizing power of $M^+$ is decreased, so species consisting of a higher ratio of $Br^-$ to $Pb^{2+}$ become more stable. Thus in the case of $PbBr_2$-NaBr, the most ideal of the systems, the position of the maximum deviation suggests, that the most predominant species present will be anions with less than four bromide ions per lead ion, e.g., $PbBr_3^-$. As the size of the alkali metal ion increases (i.e. through the series $K^+$, $Rb^+$, $Cs^+$), so the proportion of complex ions having a higher ratio of $Br^-$ to $Pb^{2+}$ will increase. Thus, in the system $PbBr_2$-CsBr, it may be inferred that $PbBr_3^-$ is not a dominant species, the deviations from ideal solution behaviour being attributed to such ions as $PbBr_4^{2-}$ and $PbBr_6^{4-}$.

It is difficult to make a direct comparison of the excess free energies of mixing with the activity results, since the errors in the calculated values of $\Delta G^E$ are relatively large, due to the integration procedure employed. Nevertheless, the above conclusions are in reasonable agreement with those deduced from the activity results, in so far as the shift of $\Delta G^E_{max.}$ to lower mole fractinns of PbBr2 with progressive increase in the size of $M^+$ is concerned.

---

1. Lantratov and Shevlyakova: Russ. J. Inorg. Chem., 6 95 (1961)

## 4A.4 ENTHALPIES

The partial molar enthalpy of lead bromide in the system $PbBr_2$-KBr (see fig. 3.6), shows an increasing negative value as the mixture becomes richer in KBr, until approximately 40 mole % $PbBr_2$. This is attributed to an increase in co-valent species in the melt. For mixtures richer in KBr, $\Delta \bar{H}_{PbBr_2}$ shows a rapid increase with composition and this can be interpreted as due to either breaking up of associated species or to the uncertainty in the experimentally determined enthalpy value for the mixture containing 19.7 mole % $PbBr_2$.

The system $PbBr_2$-RbBr (see fig. 3.12), exhibits an increased negative partial molar enthalpy for $PbBr_2$ over the whole composition range studied, whereas in mixtures of PbBr2 with CsBr (see fig.3.18), a pronounced positive value is observed over the composition range 50-100 mole % $PbBr_2$. It is questionable whether the minimum value of $\Delta \bar{H}_1$ at 70 mole % $PbBr_2$ is significant, on account of the relatively large error inherent in the calculation of this property (± 250 cals/mole). Nevertheless, the positive value for the enthalpy in this region is indicative of the breakdown of "bonded" groups and in this instance, the dissociation of lead bromide molecules is inferred (by analogy with the deviation of the activity of $PbBr_2$ in this system).

In all cases, the integral values for the enthalpy of mixing show minimum negative values, which mean that the formation of $PbBr_2$ and MBr solutions are accompanied by an evolution of heat. This is attributed to the formation of complex ions within the melt. In the

system $PbBr_2$-CsBr, the heat absorbed in the region 0.64-1.0 mole fraction $PbBr_2$, is considered to be due to the dissociation of associated $Pb^{2+}$ and $Br^-$ ions. Although the integral enthalpies, in each case, show a similar trend to that of the integral free energies, no comparison will be drawn because of the inherent inaccuracies in the calculated quantities.

## 4A.5 ENTROPIES

Associated with the formation of complex ions in molten salts, one would expect departures from random mixing in the sense of increased order; hence negative excess entropies should be observed. For the systems $PbBr_2$-RbBr and $PbBr_2$-CsBr (figs. 3.13, 3.19), this is not the case; in fact, relatively large positive values are observed especially in the $PbBr_2$-CsBr system. It has been stated[1,2], that the volume change on mixing should contribute to the excess entropy, a term of the order of $(\alpha/\beta)V^E$, where $\alpha$, is the thermal coefficient of expansion for the mixture, $\beta$, is the isothermal compressibility and $V^E$, is the excess molar volume. Information concerning $\alpha$ and $\beta$ for the systems studied is unavailable, but McCarty and Kleppa[1] have mentioned, that for ionic substances, the ratio is often of the order of 1-2 cal/deg.cm.$^3$. From the information presented by Bloom[3], the values of $V^E$ for equimolar mixtures in the systems $PbCl_2$-KCl, $PbCl_2$-RbCl and $PbCl_2$-CsCl are estimated (from a plot of molar volume versus composition) to be 0.8, 1.5 and 2.0 cm.$^3$/mole, respectively. It is assumed that the excess molar volumes are of similar magnitudes for both the binary lead bromide and lead chloride systems. Although the ratio $\alpha/\beta$ cannot be estimated exactly for these binary systems, it is evident that the

---

1. McCarty and Kleppa: J. Phys. Chem., 68 3846 (1964)
2. Scatchard: Trans. Faraday Soc., 33 160 (1937)
3. Bloom: Pure and Appl. Chem., 7 389 (1963)

contribution of the term ( $\alpha/\beta$ )$V^E$ to the entropy of mixing is large and for the two systems $PbBr_2$-RbBr and $PbBr_2$-CsBr, this is considered the major effect.

In the system $PbBr_2$-KBr (see fig. 3.7), it can be assumed, by comparison with the $PbCl_2$-KCl system, that the excess molar volume is not large and hence there appears a negative value for the excess entropy. For the system $PbBr_2$-RbBr, the initial negative excess partial molar entropy of $PbBr_2$ could be due to the formation of associations within the melt, the molar volume between 70 and 100 % $PbBr_2$ being assumed to have very nearly ideal values. At higher concentrations of alkali halide, the increased vibrational, rotational and translational entropies due to an increased excess molar volume, have a greater effect then the ordering due to complex formation and the value of $\Delta\bar{S}_1^E$ therefore, assumes an increasing positive value. The large increase in the molar volume in the system $PbBr_2$-CsBr, results in a positive excess partial molar entropy over the whole range of composition.

Owing to the error in estimation of the values of $\Delta\bar{S}_1$ and $\Delta\bar{S}_1^E$, it is doubtful whether the maxima and minima have any significance. It is interesting to note however, that a minimum appears in the partial entropy curves in each of the three systems at 50 mole % $PbBr_2$ and at 65-75 mole % $PbBr_2$ as well, in the systems $PbBr_2$-RbBr and $PbBr_2$-CsBr. These minima could be explained by an increased degree of ordering within the melt, being more predominent than the opposite effect due to the increase in molar volume, when the

concentration of associated species reached a maximum. The minima at 50 mole % $PbBr_2$, would then correspond to the complex ion $PbBr_3^-$ and that at 65-75 mole % to perhaps $Pb_2Br_5^-$. However, owing to the uncertainties in the entropy calculations, no reliance can be placed on any of the latter deductions.

## 4A.6 ACTIVITY MODELS FOR THE SYSTEMS $PbBr_2$-MBr

### a) The Hildebrand method

The theoretical derivation of activities using this model, applies in principal, to molecular liquids such as the acetone-chloroform system, where, for the formation of an equimolar compound, the following equilibrium is established[1]:

$$A + B \rightleftharpoons AB \qquad (4.a)$$

For the molten salt system $PbBr_2$-MBr a reversible equilibrium reaction for the formation of a complex of stoichiometry A:B = 1:1 may be written:

$$PbBr_2 + MBr \rightleftharpoons PbBr_3^- + M^+ \qquad (4.b)$$

or since the $M^+$ ion is not regarded as being an intimate part of the complex ion:

$$PbBr_2 + Br^- \rightleftharpoons PbBr_3^- \qquad (4.c)$$

The activity of component A (i.e. $PbBr_2$) will be given by the derived equation (see later, eqn. 4.21a), but the activity of component B (i.e. MBr) cannot be derived, since, according to reaction 4.c, component B is represented by $Br^-$ only. The activity of the alkali halide in these mixtures must therefore be obtained by the graphical integration of the Gibbs-Duhem relationship, utilising the calculated (theoretical) activity of $PbBr_2$.

---

1. Hildebrand and Scott: Solubility of Non-Electrolytes, Reinhold (1950)

(i) Calculation of the activity of $PbBr_2$, assuming the formation of the complex ion $PbBr_3^-$

Let reaction 4.c be represented as:

$$A + B \rightleftharpoons AB$$

| | | | | |
|---|---|---|---|---|
| If moles taken | = | $n_1$ | $n_2$ | |
| Then moles at equilibrium | = | $n_A(=n_1-n_{AB})$ | $n_B(=n_2-n_{AB})$ | $n_{AB}$ |
| Total number of moles | = | $n_1 + n_2 - n_{AB}$ | | |

Now assuming that the species behave in an ideal manner, i.e., they obey Raoult's law, then the mole fractions and the activities of the components are given by the equations:

$$a_1 = N_A = \frac{n_1 - n_{AB}}{n_1 + n_2 - n_{AB}} \qquad (4.15a)$$

$$a_2 = N_B = \frac{n_2 - n_{AB}}{n_1 + n_2 - n_{AB}} \qquad (4.15b)$$

$$a_3 = N_{AB} = \frac{n_{AB}}{n_1 + n_2 - n_{AB}} \qquad (4.15c.)$$

The three activity terms are related by the equilibrium constant K as follows:

$$K = \frac{a_{AB}}{a_1 \cdot a_2} \qquad (4.16)$$

Substituting in eqn. (4.16) from eqns. 4.15, we obtain:

$$K = \frac{n_{AB}(n_1 + n_2 - n_{AB})}{(n_1 - n_{AB})(n_2 - n_{AB})} \qquad (4.17)$$

To obtain a practical expression for the activity of each component, equations 4.15 must be written in terms of K, $N_1$ and $N_2$, where $N_1$ and $N_2$ are respectively, the analytical mole fractions of A and B.

From 4.15a:

$$a_1(n_1 + n_2 - n_{AB}) = n_1 - n_{AB}$$

$$a_1(n_1 - n_{AB}) + a_1 n_2 = n_1 - n_{AB}$$

$$(n_1 - n_{AB})(a_1 - 1) + a_1 n_2 = 0$$

$$n_1 - n_{AB} = - \frac{a_1 n_2}{a_1 - 1} \qquad (4.18)$$

Substitute (4.18) in (4.17):

$$K = \frac{n_{AB} \left[ n_2 - \frac{a_1 n_2}{a_1 - 1} \right]}{- (n_2 - n_{AB}) \frac{a_1 n_2}{a_1 - 1}}$$

$$= \frac{n_{AB}(- n_2)}{- (n_2 - n_{AB}) a_1 n_2}$$

$$= \frac{n_{AB}}{a_1 (n_2 - n_{AB})}$$

On rearranging:

$$n_{AB} = \frac{K a_1 n_2}{1 + K a_1} \qquad (4.19)$$

Substitute (4.19) in (4.15a):

$$a_1 = \frac{n_1 - \left[ \frac{K a_1 n_2}{1 + K a_1} \right]}{n_1 + n_2 - \left[ \frac{K a_1 n_2}{1 + K a_1} \right]}$$

$$= \frac{n_1(1 + K a_1) - K a_1 n_2}{(n_1 + n_2)(1 + K a_1) - K a_1 n_2}$$

$$a_1 \left[ (n_1 + n_2)(1 + K a_1) - K a_1 n_2 \right] = n_1(1 + K a_1) - K a_1 n_2$$

Divide both sides by $(n_1 + n_2)$:

$$a_1 \left[ 1 + K a_1 - \frac{K a_1 n_2}{n_1 + n_2} \right] = \frac{n_1(1 + K a_1)}{n_1 + n_2} - \frac{K a_1 n_2}{n_1 + n_2}$$

$$a_1 (1 + K a_1 - N_2 K a_1) = N_1(1 + K a_1) - N_2 K a_1$$

which on rearrangement gives:

$$K = \frac{N_1 - a_1}{a_1 [N_2(1 - a_1) - (N_1 - a_1)]} \qquad (4.20)$$

Similar expressions can be derived in terms of $a_2$ and $a_{AB}$ for the other equilibrium components.

Eqn. 4.20 has been solved for $a_1$ in terms of $N_1$, $N_2$ and K by Hildebrand[1], i.e.:

$$a_1 = \frac{k N_1 - 2 + 2(1 - k N_1 N_2)^{\frac{1}{2}}}{k N_1} \qquad (4.21a)$$

and similarly for $a_2$ and $a_{AB}$, i.e.:

$$a_2 = \frac{k N_2 - 2 + 2(1 - k N_1 N_2)^{\frac{1}{2}}}{k N_2} \qquad (4.21b)$$

$$a_{AB} = \frac{2 - k N_1 N_2 - 2(1 - k N_1 N_2)^{\frac{1}{2}}}{k N_1 N_2} \qquad (4.21c)$$

where $k = \frac{4K}{(K + 1)}$

By using as reference point the experimental activity at 50 mole % $PbBr_2$ (corresponding to the stoichiometric composition of the ion $PbBr_3^-$), as obtained from the plot of $a_{PbBr_2}$ versus composition, the association constant for the reaction $PbBr_2 + Br^- \rightleftharpoons PbBr_3^-$, can be estimated for each system, using equation 4.20. By substituting this value of K in equation 4.21a, the value of $a_{PbBr_2}$ can be calculated over the whole range of composition. The experimental and theoretically determined activities for each system are compared in Table 4.7 and are illustrated in figs. 4.2, 3, 4.

---

1. Hildebrand and Scott: Solubility of Non-Electrolytes, Reinhold, (1950)

TABLE 4.7

Comparison of experimental activities of $PbBr_2$ with those derived using the Hildebrand method and assuming the complex ion $PbBr_3^-$

| system | K | m.f. $PbBr_2$ | Exptl. activity | Hildebrand activity | Deviation of Hildebrand activity from exptl. activity |
|---|---|---|---|---|---|
| $PbBr_2$-KBr | 6.018 | 0.2 | 0.046 | 0.043 | - 0.003 |
| | | 0.3 | 0.072 | 0.084 | + 0.012 |
| | | 0.4 | 0.123 | 0.155 | + 0.032 |
| | | 0.5 | 0.274 | 0.274 | 0.000 |
| | | 0.6 | 0.517 | 0.437 | - 0.080 |
| | | 0.7 | 0.655 | 0.608 | - 0.047 |
| | | 0.8 | 0.770 | 0.761 | - 0.009 |
| | | 0.9 | 0.884 | 0.891 | + 0.007 |
| $PbBr_2$-RbBr | 13.81 | 0.2 | 0.020 | 0.021 | + 0.001 |
| | | 0.3 | 0.046 | 0.045 | - 0.001 |
| | | 0.4 | 0.100 | 0.093 | - 0.007 |
| | | 0.5 | 0.205 | 0.206 | + 0.001 |
| | | 0.6 | 0.380 | 0.396 | + 0.016 |
| | | 0.7 | 0.579 | 0.591 | + 0.012 |
| | | 0.8 | 0.749 | 0.755 | + 0.006 |
| | | 0.9 | 0.892 | 0.890 | - 0.002 |
| $PbBr_2$-CsBr | 11.12 | 0.2 | 0.011 | 0.026 | + 0.015 |
| | | 0.3 | 0.033 | 0.053 | + 0.020 |
| | | 0.4 | 0.088 | 0.108 | + 0.020 |
| | | 0.5 | 0.224 | 0.223 | - 0.001 |
| | | 0.6 | 0.387 | 0.405 | + 0.018 |
| | | 0.7 | 0.570 | 0.594 | + 0.024 |
| | | 0.8 | 0.796 | 0.757 | - 0.039 |
| | | 0.9 | 0.947 | 0.890 | - 0.057 |

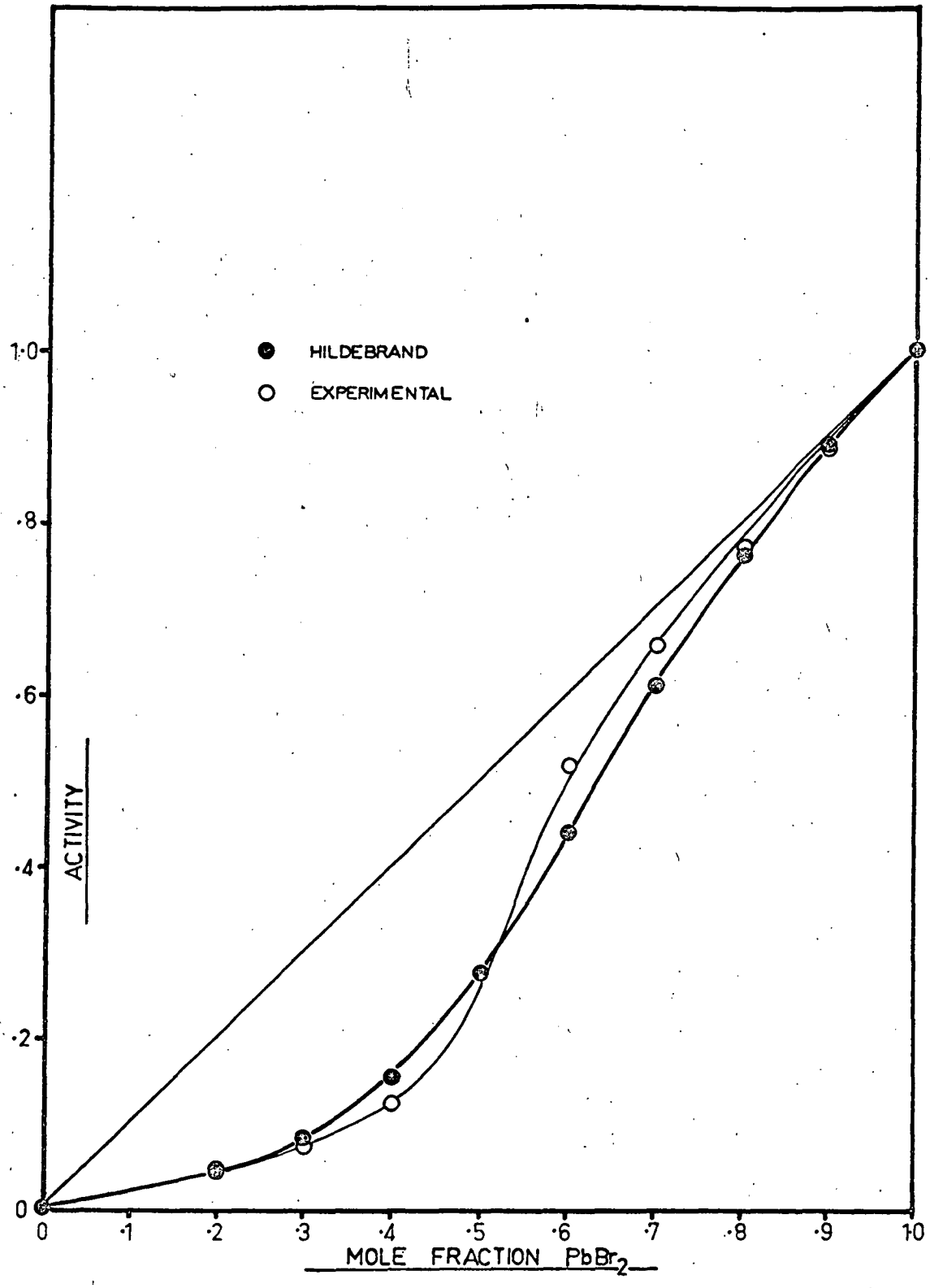
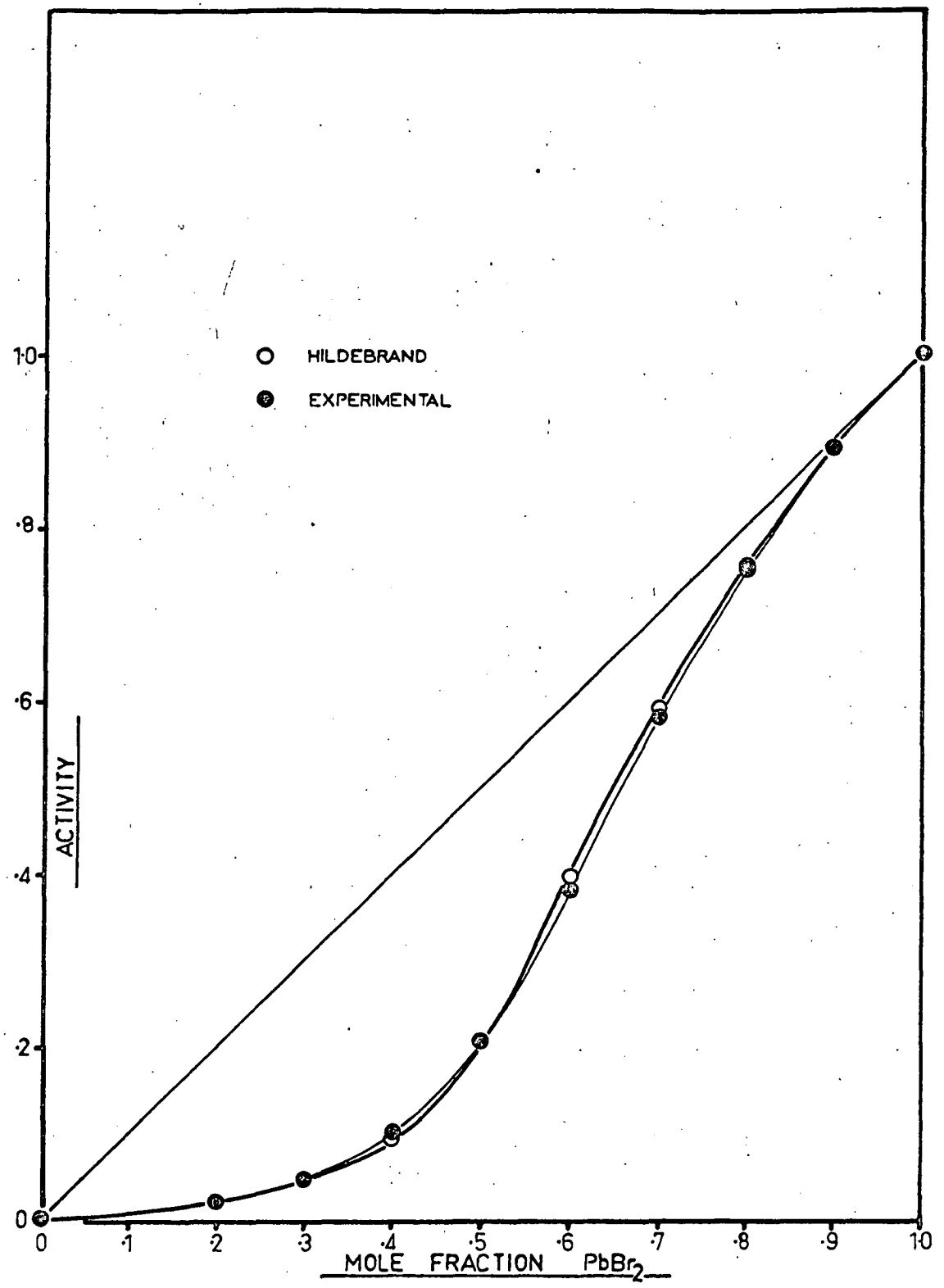



FIG. 4·2

SYSTEM $PbBr_2$–KBr (600°C)
COMPARISON OF HILDEBRAND AND EXPTL. ACTIVITIES OF $PbBr_2$




SYSTEM $PbBr_2$ – RbBr (600°C)

FIG. 4·3 COMPARISON OF HILDEBRAND AND EXPTL. ACTIVITIES OF $PbBr_2$

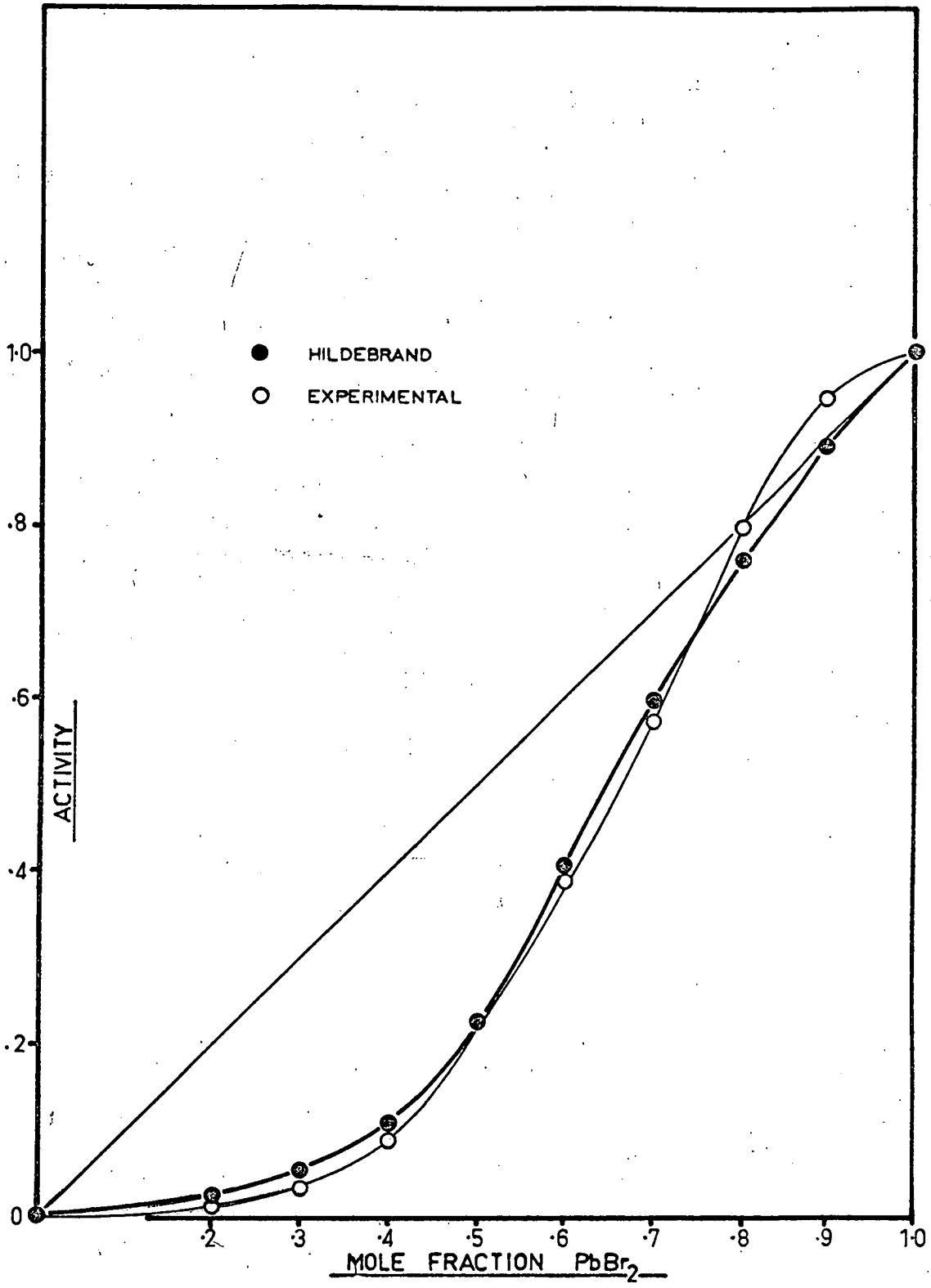



FIG. 4·4

SYSTEM $PbBr_2$–CsBr (600°C)

COMPARISON OF HILDEBRAND AND EXPTL. ACTIVITIES OF $PbBr_2$

Agreement between theoretical and experimental curves is reasonable and in the case of the system $PbBr_2$-RbBr it is very good. From the values of K, it can be seen that the stability of the ion $PbBr_3^-$ is proportional to the deviations of $a_{PbBr_2}$ from the ideal Temkin line at 50 mole % $PbBr_2$. For both systems $PbBr_2$-KBr and $PbBr_2$-CsBr, the positive deviations of the Hildebrand activities from the experimental activities in the region 30-40 mole % $PbBr_2$, indicate that species having a greater number of $Br^-$ ions per $Pb^{2+}$ ion, compared to $PbBr_3^-$, are present.

(ii) Calculation of the activity of $PbBr_2$, assuming the formation of the complex ion $PbBr_4^{2-}$

| | | | | | | |
|---|---|---|---|---|---|---|
| Let the reaction | | $PbBr_2$ | + | $2Br^-$ | $\longrightarrow$ | $PbBr_4^{2-}$ |
| be represented as: | | A | + | 2B | $\longrightarrow$ | $AB_2$ |
| If moles taken | = | $n_1$ | | $n_2$ | | |
| Then moles at equilibrium | = | $(n_1 - n_{AB_2})$ | | $(n_2 - 2n_{AB_2})$ | | $n_{AB_2}$ |
| Total number of moles | = | $n_1 + n_2 - 2n_{AB_2}$ | | | | |

Assuming the species behave in an ideal manner as before, then the activities are given by the following equations:

$$a_1 = \frac{n_1 - n_{AB_2}}{n_1 + n_2 - 2n_{AB_2}} \qquad (4.22a)$$

$$a_2 = \frac{n_2 - 2n_{AB_2}}{n_1 + n_2 - 2n_{AB_2}} \qquad (4.22b)$$

$$a_{AB_2} = \frac{n_{AB_2}}{n_1 + n_2 - 2n_{AB_2}} \qquad (4.22c)$$

Hence: $$K = \frac{a_{AB_2}}{a_1 \cdot a_2^2}$$

$$\text{i.e.} \quad K = \frac{n_{AB_2}(n_1 + n_2 - 2n_{AB_2})^2}{(n_1 - n_{AB_2})(n_2 - 2n_{AB_2})^2} \tag{4.23}$$

From eqn. 4.22a:

$$a_1 = \frac{n_1 - n_{AB_2}}{(n_1 - n_{AB_2}) + (n_2 - n_{AB_2})}$$

which on rearrangement gives:

$$(n_1 - n_{AB_2}) = -\frac{a_1}{a_1 - 1}(n_2 - n_{AB_2}) \tag{4.24}$$

Substitute (4.24) in (4.23):

$$K = \frac{n_{AB_2}\left[(n_2 - n_{AB_2}) - \frac{a_1}{a_1 - 1}(n_2 - n_{AB_2})\right]^2}{-\frac{a_1}{a_1 - 1}(n_2 - n_{AB_2})(n_2 - 2n_{AB_2})^2}$$

$$= \frac{n_{AB_2}(n_2 - n_{AB_2})\left[-\frac{1}{a_1 - 1}\right]^2}{-\frac{a_1}{a_1 - 1}(n_2 - 2n_{AB_2})^2}$$

$$= \frac{n_{AB_2}(n_2 - n_{AB_2})}{-a_1(a_1 - 1)(n_2 - 2n_{AB_2})^2} \tag{4.25}$$

From (4.22a):

$$a_1(n_1 + n_2) - 2n_{AB_2}a_1 = n_1 - n_{AB_2}$$

$$n_{AB_2} = \frac{a_1(n_1 + n_2) - n_1}{(2a_1 - 1)} \tag{4.26}$$

Substitute (4.26) in (4.25):

$$K = \frac{\frac{a_1(n_1 + n_2) - n_1}{(2a_1 - 1)}\left[n_2 - \frac{a_1(n_1 + n_2) - n_1}{(2a_1 - 1)}\right]}{-a_1(a_1 - 1)\left[n_2 - \frac{2a_1(n_1 + n_2) - 2n_1}{(2a_1 - 1)}\right]^2}$$

which on rearrangement gives:

$$K = \frac{\left[a_1 (n_1 + n_2) - n_1\right]\left[n_2 (a_1 - 1) - n_1 (a_1 - 1)\right]}{- a_1 (a_1 - 1)(2n_1 - n_2 - 2n_1 a_1)^2}$$

$$= \frac{\left[a_1 (n_1 + n_2) - n_1\right]\left[n_2 - n_1\right]}{- a_1 (2n_1 - n_2 - 2n_1 a_1)^2}$$

By dividing nominator and denominator of this equation by $(n_1 + n_2)^2$ and substituting values for $n_1$ and $n_2$, where:

$$N_1 = \frac{n_1}{n_1 + n_2} \quad \text{and} \quad N_2 = \frac{n_2}{n_1 + n_2},$$

the final expression for K is obtained:

$$K = \frac{(N_1 - a_1)(N_2 - N_1)}{a_1 \left[2N_1 (1 - a_1) - N_2\right]^2} \qquad (4.27)$$

It is worth noting, that whereas the equilibrium between A, B and AB produces negative deviations from the ideal activity over the whole composition range, the present equilibrium, i.e. $A + 2B \rightleftharpoons AB_2$, produces negative deviations of $a_1$ when $N_1 < N_2$ and positive deviations when $N_1 > N_2$. When the experimental activities of $PbBr_2$, at different compositions, are closely approximated by the calculated Hildebrand activities, the value of K, for the association constant of the complex ion, is virtually independent of the composition chosen as reference point. When there is a large discrepancy between experimental and theoretical values for most of the compositions between 0 and 100 mole % $PbBr_2$, the composition chosen as reference point is found to be very critical for the value of K obtained. If

the value of the activity at $N_1 = 0.33$, $N_2 = 0.67$ is chosen, then subsequent values of $a_{PbBr_2}$ for mole fractions of $N_1 < 0.33$ show pronounced negative deviations from the experimental curve. If on the other hand, the reference point $N_1 = 0.25$, $N_2 = 0.75$ is chosen, then although for $N_1 < 0.25$ a greater similarity is shown, the value of K so determined is far different. Because it is difficult to obtain accurate quantitative information using the association scheme for $PbBr_4^{2-}$, the theoretical activities for this complex ion will only be discussed in a qualitative manner.

To obtain an expression for $a_1$, in terms of K, $N_1$ and $N_2$ from eqn. 4.27, a complex cubic equation must be solved and hence to determine $a_1$, for compositions other than the reference point, a trial and error procedure was used. The value of the association constant for $PbBr_4^{2-}$ has been calculated for each of the three binary systems, using as reference point the composition $N_1 = 0.25$, $N_2 = 0.75$. The results are summarized in Table 4.8. It is to be noted, that when $N_1 > N_2$, two values for $a_{PbBr_2}$ are possible, depending on whether $2N_1(1-a_1) > N_2$ or $2N_1(1 - a_1) < N_2$. The values in Table 4.8 are calculated for $2N_1(1 - a_1) > N_2$. In Table 4.9 and fig. 4.5, are represented the magnitude of the association constant and the activities for $PbBr_2$ for the system PbBr2-RbBr at the two reference points ($N_1 = 0.25$ and $N_1 = 0.33$).

The activities calculated assuming the association scheme 4.d, explain two phenomena in the deviations of the Hildebrand activity for $PbBr_2$, assuming the complex ion $PbBr_3^-$, from the experimental activities:

TABLE 4.8

Comparison of experimental activities of $PbBr_2$ with those derived using the Hildebrand association scheme for the complex $PbBr_4^{2-}$, at the reference point $N_1 = 0.25$, $N_2 = 0.75$

| system | association constant | m.f. $PbBr_2$ | Exptl. activity | Hildebrand activity | $\Delta a^*$ |
|---|---|---|---|---|---|
| $PbBr_2$-KBr | 23.0 | 0.1 | 0.023 | 0.006 | - 0.017 |
| | | 0.2 | 0.072 | 0.027 | - 0.045 |
| | | 0.25 | 0.057 | 0.055 | - 0.002 |
| | | 0.3 | 0.072 | 0.113 | + 0.041 |
| | | 0.4 | 0.123 | 0.275 | + 0.152 |
| | | 0.5 | 0.274 | 0.500 | + 0.226 |
| $PbBr_2$-RbBr | 42.9 | 0.1 | 0.006 | 0.004 | - 0.002 |
| | | 0.2 | 0.020 | 0.015 | - 0.005 |
| | | 0.25 | 0.033 | 0.035 | + 0.002 |
| | | 0.3 | 0.046 | 0.100 | + 0.054 |
| | | 0.4 | 0.100 | 0.300 | + 0.200 |
| | | 0.5 | 0.205 | 0.500 | + 0.295 |
| $PbBr_2$-CsBr | 80.35 | 0.1 | 0.002 | 0.002 | 0.000 |
| | | 0.2 | 0.011 | 0.009 | - 0.002 |
| | | 0.25 | 0.019 | 0.021 | + 0.002 |
| | | 0.3 | 0.033 | 0.061 | + 0.028 |
| | | 0.4 | 0.088 | 0.184 | + 0.096 |
| | | 0.5 | 0.224 | 0.500 | + 0.276 |

* Deviation of the Hildebrand activity from the experimental activity.

1) In the region of 30-40 mole % $PbBr_2$ in the systems $PbBr_2$-KBr and $PbBr_2$-CsBr, the lower experimental value for $a_{PbBr_2}$ can be attributed to the complex species $PbBr_4^{2-}$. This is not unequivocal however, as other association schemes involving, for example, such ions

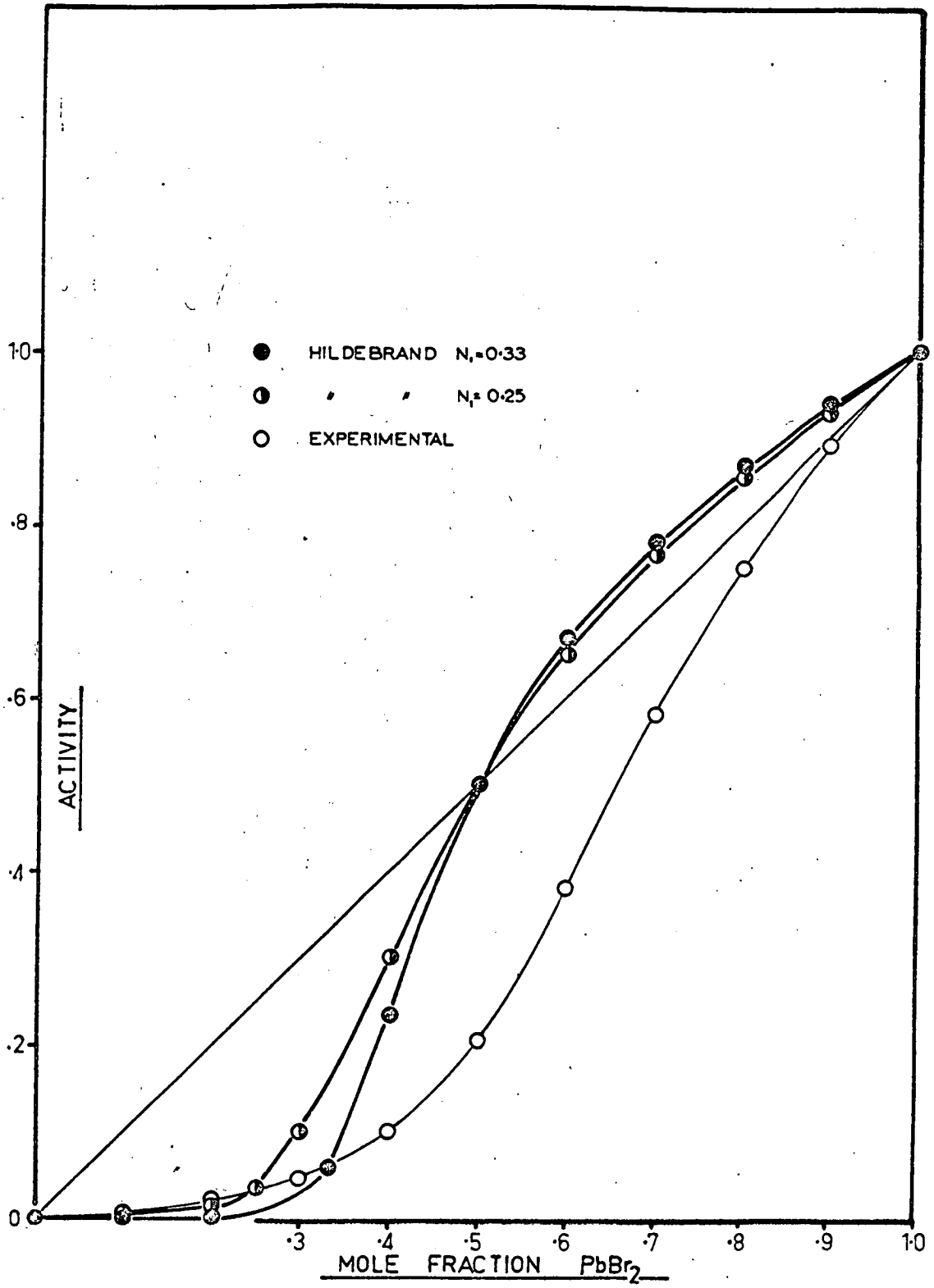



FIG. 4·5

SYSTEM $PbBr_2$–RbBr (600°C)

COMPARISON OF HILDEBRAND ACTIVITIES FOR $PbBr_2$ AT THE REFERENCE PTS. $N_1 = 0{\cdot}25, 0{\cdot}33$.

ASSUMING THE COMPLEX ION $PbBr_4^{2-}$

TABLE 4.9

Comparison of the Hildebrand activities assuming the complex $PbBr_4^{2-}$ at the two reference points, $N_1 = 0.25$ and $N_1 = 0.33$ for the system $PbBr_2$-RbBr (600°C)

| composition m.f.$PbBr_2$ | $a_{PbBr_2}$ ref. pt. : $N_1 = 0.25$ | $a_{PbBr_2}$ ref. pt. : $N_1 = 0.33$ |
|---|---|---|
| 0.10 | 0.004 | 0.000 |
| 0.20 | 0.015 | 0.001 |
| 0.25 | 0.035 | - |
| 0.30 | 0.100 | - |
| 0.33 | - | 0.060 |
| 0.40 | 0.300 | 0.235 |
| 0.50 | 0.500 | 0.500 |
| 0.60 | 0.650 | 0.670 |
| 0.70 | 0.765 | 0.780 |
| 0.80 | 0.856 | 0.870 |
| 0.90 | 0.930 | 0.940 |
| Association constant: | 42.9 | 904.0 |

as $PbBr_5^{3-}$, $Pb_2Br_5^{-}$, $PbBr_6^{4-}$, etc., could well produce such deviations in this range of composition. However, the complexity of the calculations involved put such models outside the scope of this discussion.

2) The positive deviation of $a_{PbBr_2}$ from the ideal Temkin value between 80-100 mole % $PbBr_2$ in the system $PbBr_2$-CsBr, can also be attributed to the presence of species such as $PbBr_4^{2-}$ on the basis of this model.

It is quite conceivable, that a combination of both these association schemes may provide theoretical activities which would coincide with those determined experimentally. This of course necessitates the assumption that both species $PbBr_3^-$ and $PbBr_4^{2-}$, are present in the melt.

b) The Bredig method

In this essentially "ionic" model, the formation of complexes with infinite stability constants are assumed[1]. A similar approach has been used by Beusman[2]. Because only the final activity equations were presented by Bredig, the following derivation of the general equations has been presented by the present author.

Consider the general reaction for the binary system $AX_2 + MX$:

$$AX_2 + (z - 2)\,X^- \rightleftharpoons AX_z^{(z-2)-} \qquad (4.e)$$

where $AX_2$ is a divalent metal halide, $(z - 2)X^-$ is the halide ions contributed by the alkali halide and z is the number of halide ligands per divalent metal ion.

Now, if the reaction goes to completion, then the activity of $AX_2$ will only have a value greater than zero when $N_1 > 1/(z - 1)$ and the activity of MX will be greater than zero only when $N_1 < 1/(z - 1)$. Here $N_1$ is the mole fraction of $AX_2$ and $N_2$ is the mole fraction of MX. From the Temkin equation relating composition and activity, we have:

---

1. Bredig: J. Chem. Phys., 37 451 (1962)
2. Beusman: U.S. Atomic Energy Comm., ORNL 2323 (1957)

$$a_{AX_2} = N_A^{2+} . (N_X^-)^2 . \gamma_{AX_2} \quad (4.28)$$

$$a_{MX} = N_M^+ . N_X^- . \gamma_{MX} \quad (4.29)$$

where $\gamma_{AX_2}$ and $\gamma_{MX}$ = activity coefficients of $AX_2$ and MX respectively

" $N_A^{2+}$ = cationic fraction of $A^{2+}$

$$= \frac{n_A^{2+}}{n_A^{2+} + n_M^+}$$

" $N_M^+$ = cationic fraction of $M^+$

$$= \frac{n_M^+}{n_M^+ + n_A^{2+}}$$

" $N_X^-$ = anionic fraction of $X^-$

$$= \frac{n_X^-}{n_X^- + n_{AX_2}(z - 2)^-}$$

" $n_a$ = no. of gm. ions of species "a" present.

(i) Determination of $a_{MX}$

Since $a_{MX}$ is only greater than zero when $N_1 < 1/(z - 1)$, then we must only consider the case when excess MX is present above the quantity required to remove all the free $AX_2$ as the complex species $AX_z(z - 2)^-$.

Now $$N_M^+ = \frac{n_M^+}{n_M^+ + n_A^{2+}} = \frac{n_M^+}{n_M^+ + 0} = 1$$

$$N_X^- = \frac{n_X^-}{n_X^- + n_{AX_z}(z - 2)^-}$$

$$= \frac{N_2 - (z - 2)(1 - N_2)}{N_2 - (z - 2)(1 - N_2) + (1 - N_2)}$$

$$= \frac{1 - (z - 1)(1 - N_2)}{1 - (z - 2)(1 - N_2)}$$

where $N_2$ = mole fraction of MX

and where $1-N_2$ = mole fraction of $AX_2$

Now $$a_{MX} = N_{M^+} \cdot N_{X^-} \cdot \gamma_{MX}$$

Assume that $\gamma_{MX} = 1$

In which case:

$$a_{MX} = \frac{1 - (z - 1)(1 - N_2)}{1 - (z - 2)(1 - N_2)} \qquad (4.30)$$

(ii) Determination of $a_{MX_2}$

Because $a_{AX_2}$ is only greater than zero when $N_1 > 1/(z - 1)$, then only the case when excess $AX_2$ is present above the quantity required to remove all the free MX as the complex species $AX_z(z - 2)^-$ can be considered.

Now $$N_{A^{2+}} = \frac{n_{A^{2+}}}{n_{A^{2+}} + n_{M^+}} = \frac{(1 - N_2) - \frac{1}{(z - 2)} \cdot N_2}{(1 - N_2) - \frac{1}{(z - 2)} \cdot N_2 + N_2}$$

$$= \frac{(1 - N_2)(z - 2) - N_2}{(1 - N_2)(z - 2) - N_2 + N_2(z - 2)}$$

$$= \frac{(z - 2) - (z - 1)\, N_2}{(z - 2) - N_2}$$

$$N_{X^-} = \frac{n_{X^-}}{n_{X^-} + n_{AX_z(z - 2)^-}} = \frac{2(1 - N_2) - \frac{2}{z - 2} \cdot N_2}{2(1 - N_2) - \frac{1}{z - 2} \cdot N_2}$$

$$= \frac{2(z - 2)(1 - N_2) - 2N_2}{2(z - 2)(1 - N_2) - N_2}$$

$$= \frac{(2z - 4) - (2z - 2)\, N_2}{(2z - 4) - (2z - 3)\, N_2}$$

Now $$a_{AX_2} = N_{A^{2+}} \cdot (N_{X^-})^2 \cdot \gamma_{AX_2}$$

Assume that $\gamma_{AX_2} = 1$

In which case:

$$a_{AX_2} = \frac{(z-2) - (z-1)\,N_2}{(z-2) - N_2} \left[\frac{(2z-4) - (2z-2)\,N_2}{(2z-4) - (2z-3)\,N_2}\right]^2 \quad (4.31)$$

Calculated values for $a_{AX_2}$ and $a_{MX}$ for different mole fractions of $PbBr_2$ are shown in Table 4.10, for three different values of z, namely, z = 3, 4 and 6, which correspond to the complex ions $PbBr_3^-$, $PbBr_4^{2-}$ and $PbBr_6^{4-}$.

The above expressions for $a_{MX}$ and $a_{AX_2}$ are calculated on the basis of the Temkin ion fractions. A similar set of expressions can be calculated on the basis of the Flood et al. equation, relating composition and activity[1,2], i.e.

$$a_{AX_2} = N'_{A^{2+}} \cdot (N'_{X^-})^2 \cdot \gamma_{AX_2} \quad (4.32)$$

$$a_{MX} = N'_{M^+} \cdot N'_{X^-} \cdot \gamma_{MX} \quad (4.33)$$

where N'a = Equivalent ionic fraction of "a" and is given by:

$$N'_{A^{2+}} = \frac{n_{A^{2+}}}{n_{A^{2+}} + \frac{1}{2}n_{M^+}}$$

$$N'_{M^+} = \frac{\frac{1}{2}n_{M^+}}{\frac{1}{2}n_{M^+} + n_{A^{2+}}}$$

$$N'_{X^-} = \frac{\frac{1}{(z-2)}\,n_{X^-}}{\frac{1}{(z-2)}\,n_{X^-} + n_{AX_z}(z-2)-}$$

---

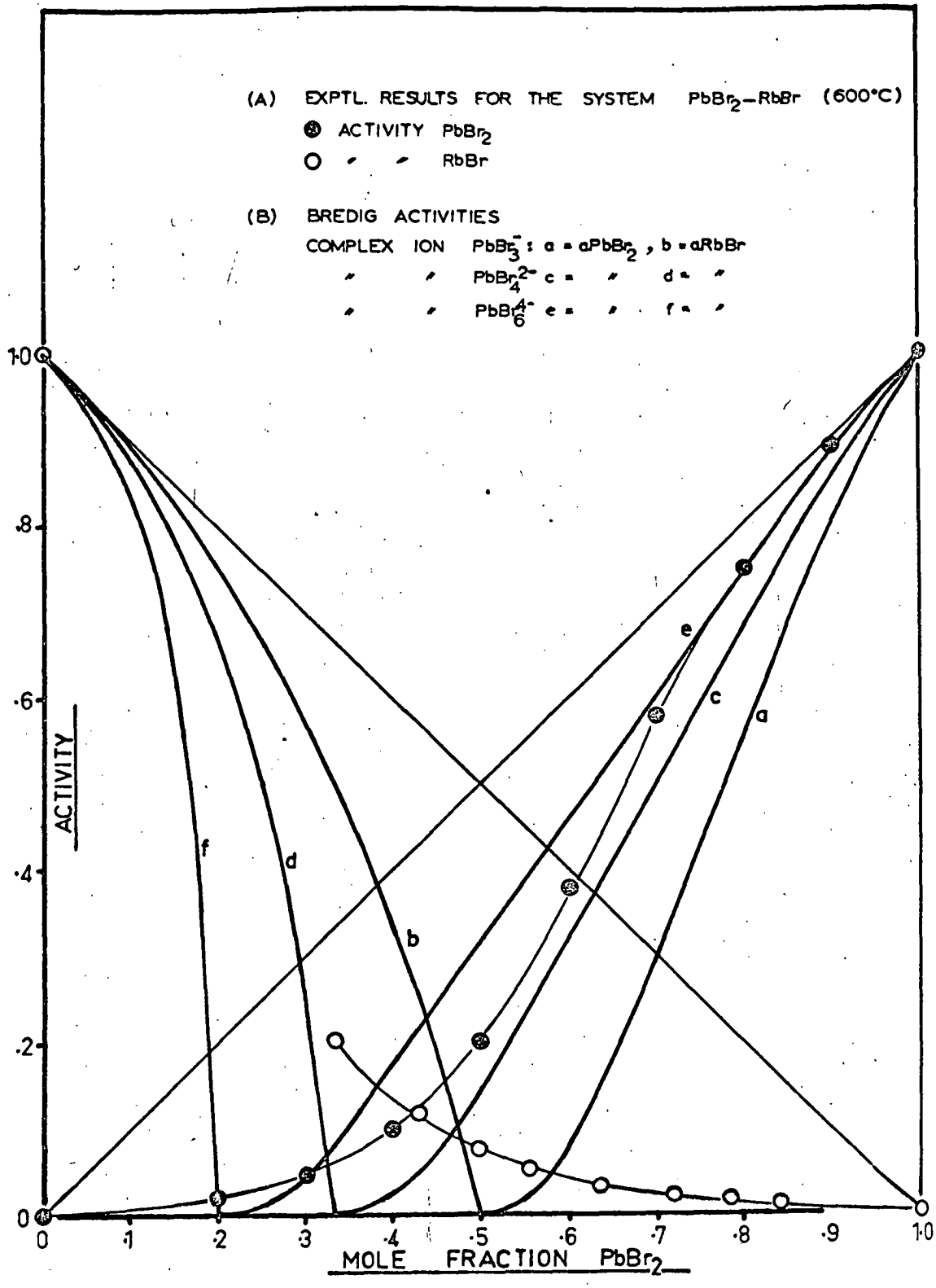
1. Flood, Førland and Grjotheim: Inst. Min. Met. Symp., Molten Slags, (1953)

2. Flood, Førland and Grjotheim: Z. anorg. u allgem. Chem., 276 289 (1954)

TABLE 4.10

Values for $a_{AX_2}$ and $a_{MX}$ (calculated using Temkin ion fractions) for different compositions of the system $AX_2$ - MX - Bredig Model

| z | mole fraction $AX_2$ | $a_{AX_2}$ | mole fraction $AX_2$ | $a_{MX}$ |
|---|---|---|---|---|
| 3 | 0.50 | 0.000 | 0.00 | 1.000 |
| | 0.55 | 0.017 | 0.10 | 0.889 |
| | 0.60 | 0.083 | 0.20 | 0.750 |
| | 0.65 | 0.184 | 0.30 | 0.571 |
| | 0.70 | 0.302 | 0.35 | 0.462 |
| | 0.80 | 0.551 | 0.40 | 0.333 |
| | 0.90 | 0.787 | 0.45 | 0.182 |
| | 0.95 | 0.897 | 0.50 | 0.000 |
| | 1.00 | 1.000 | | |
| 4 | 0.33 | 0.000 | 0.00 | 1.000 |
| | 0.40 | 0.023 | 0.05 | 0.944 |
| | 0.50 | 0.148 | 0.10 | 0.875 |
| | 0.60 | 0.320 | 0.15 | 0.786 |
| | 0.70 | 0.501 | 0.20 | 0.667 |
| | 0.80 | 0.678 | 0.25 | 0.500 |
| | 0.90 | 0.844 | 0.30 | 0.250 |
| | 1.00 | 1.000 | 0.33 | 0.000 |
| 6 | 0.20 | 0.000 | 0.00 | 1.000 |
| | 0.25 | 0.012 | 0.05 | 0.938 |
| | 0.30 | 0.052 | 0.10 | 0.833 |
| | 0.40 | 0.174 | 0.12 | 0.769 |
| | 0.50 | 0.315 | 0.14 | 0.682 |
| | 0.60 | 0.459 | 0.16 | 0.556 |
| | 0.70 | 0.601 | 0.18 | 0.357 |
| | 0.80 | 0.739 | 0.20 | 0.000 |
| | 0.90 | 0.872 | | |




SYSTEM $PbBr_2$–RbBr

FIG. 4.6 THEORETICAL BREDIG ACTIVITIES (TEMKIN ION FRACTIONS)

(iii) Determination of $a_{MX}$ using Flood et al. ion fractions

$$N'_{M^+} = 1 \text{ (as before)}$$

$$N'_{X^-} = \frac{\frac{N_2}{z-2} - \frac{(z-2)(1-N_2)}{(z-2)}}{\frac{N_2 - (z-2)(1-N_2)}{(z-2)} + (1-N_2)}$$

$$= \frac{N_2 - (z-2)(1-N_2)}{N_2}$$

$$= \frac{1 - (z-1)(1-N_2)}{N_2}$$

From 4.33, assuming $\gamma_{MX} = 1$, we have:

$$a_{MX} = \frac{1 - (z-1)(1-N_2)}{N_2} \qquad (4.34)$$

(iv) Determination of $a_{AX_2}$ using Flood et al. ion fractions

$$= \frac{n_{A^{2+}}}{n_{A^{2+}} + \frac{1}{2}n_{M^+}} = \frac{(1-N_2) - \frac{1}{(z-2)}\cdot N_2}{(1-N_2) - \frac{1}{(z-2)}\cdot N_2 + \frac{1}{2}N_2}$$

$$= \frac{(z-2) - (z-1)\,N_2}{(z-2) - \frac{1}{2}N_2 z}$$

$$= \frac{\frac{1}{(z-2)}\cdot n_{X^-}}{\frac{1}{(z-2)}\cdot n_{X^-} + n_{AX_z}(z-2)-}$$

$$= \frac{\frac{1}{(z-2)}\left[2(1-N_2) - \frac{2}{(z-2)}\cdot N_2\right]}{\frac{1}{(z-2)}\left[2(1-N_2) - \frac{2}{(z-2)}\cdot N_2\right] + \frac{1}{(z-2)}\,N_2}$$

$$= \frac{2(z-2)(1-N_2) - 2N_2}{2(z-2)(1-N_2) - 2N_2 + N_2\,(z-2)}$$

$$= \frac{(z-2) - (z-1)\,N_2}{(z-2) - \frac{1}{2}N_2 z}$$

From 4.32, assuming $\gamma_{AX_2} = 1$, we have:

$$a_{AX_2} = \left[ \frac{(z - 2) - (z - 1)\, N_2}{(z - 2) - \frac{1}{2} N_2 z} \right]^3 \qquad (4.35)$$

Values for $a_{AX_2}$ and $a_{MX}$, on the basis of the Flood et al. relationship between activity and composition, for different mole fractions of $AX_2$, are presented in Table 4.11. Theoretical activities for $AX_2$ (e.g. $PbBr_2$) and MBr using both Temkin and Flood et al. ion fractions, are represented in figs. 4.6 and 4.7. Of the two methods of calculation of $a_{AX_2}$ and $a_{MX}$, eqns. 4.30 and 4.31 probably give the best representation. It is generally accepted that the Temkin ion fractions are applicable with least error to simple binary mixtures such as the systems $PbBr_2$-MBr, whereas the equivalent ion fractions of Flood et al. are really only applicable to reciprocal molten salt systems (see Section 1.5b).

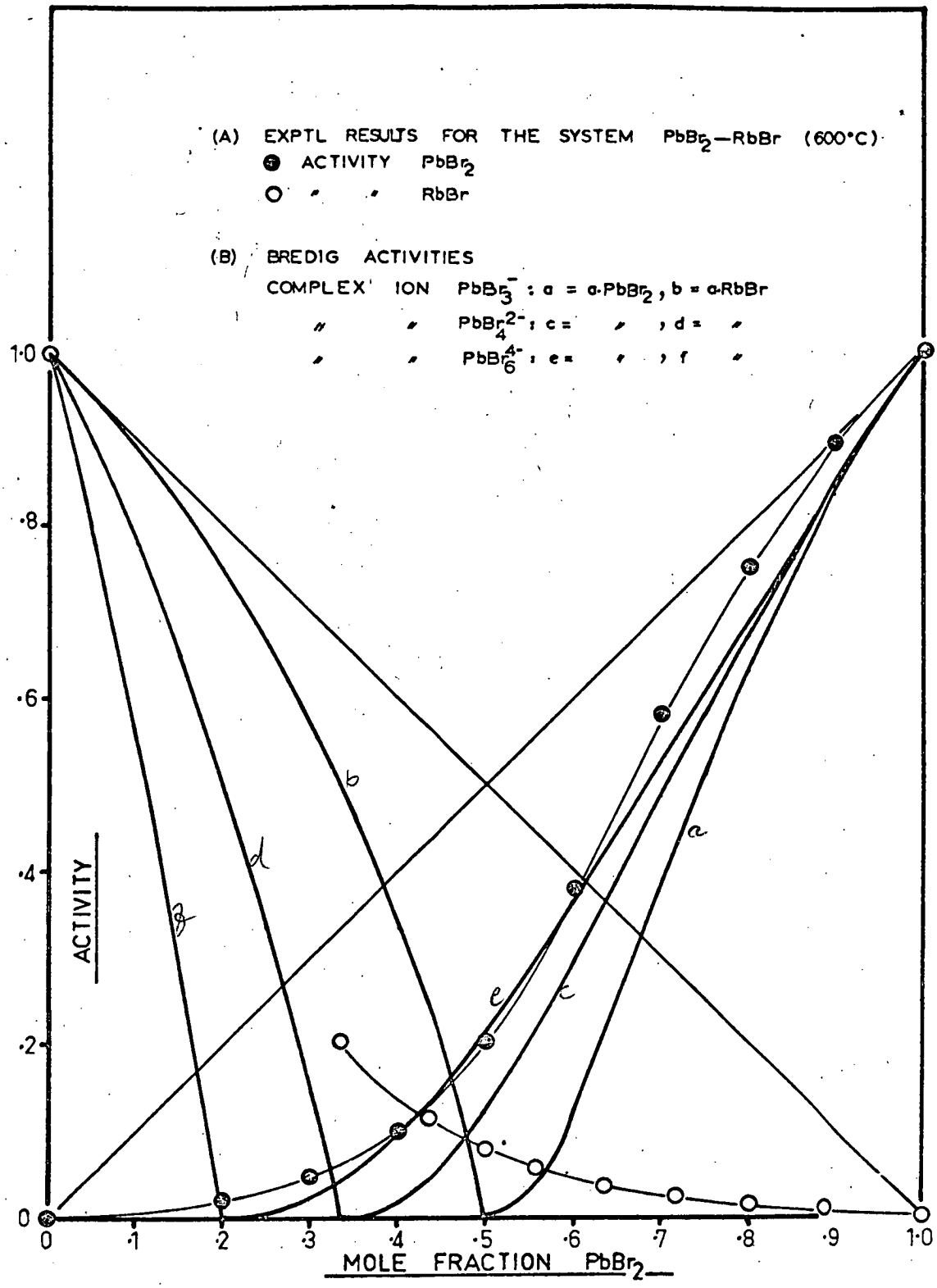
Provided the experimental activity isotherm shows a positive deviation from that calculated theoretically for a particular complex ion, then the deviation of the experimentally determined activities from ideal values can be attributed in part, if not wholly, to the presence of this complex. The theoretical line for each value of z, represents the maximum deviation possible at each composition for that species. If the experimental activity has a lower value than that calculated for a given z (e.g. z = m), then either the compound $AX_m^{(m-2)-}$ is not present, or else it is present in conjunction with another species.

As this model is applicable to both components, the Gibbs-Duhem relationship must also apply and the species $AX_m^{(m-2)-}$ must show

TABLE 4.11

Values for $a_{AX_2}$ and $a_{MX}$ (calculated using Flood et al. ion fractions) for different compositions of the system $AX_2$-MBr - Bredig model

| z | mole fraction $AX_2$ | $a_{AX_2}$ | mole fraction $AX_2$ | $a_{MX}$ |
|---|---|---|---|---|
| 3 | 0.50 | 0.000 | 0.00 | 1.000 |
| | 0.55 | 0.029 | 0.10 | 0.889 |
| | 0.60 | 0.125 | 0.20 | 0.750 |
| | 0.65 | 0.252 | 0.30 | 0.571 |
| | 0.70 | 0.385 | 0.35 | 0.462 |
| | 0.75 | 0.512 | 0.40 | 0.333 |
| | 0.80 | 0.630 | 0.45 | 0.182 |
| | 0.90 | 0.834 | 0.50 | 0.000 |
| 4 | 0.33 | 0.000 | 0.00 | 1.000 |
| | 0.40 | 0.016 | 0.05 | 0.895 |
| | 0.45 | 0.059 | 0.10 | 0.778 |
| | 0.50 | 0.125 | 0.15 | 0.647 |
| | 0.60 | 0.296 | 0.20 | 0.500 |
| | 0.70 | 0.485 | 0.25 | 0.333 |
| | 0.75 | 0.579 | 0.30 | 0.143 |
| | 0.80 | 0.670 | 0.33 | 0.000 |
| | 0.85 | 0.758 | | |
| | 0.90 | 0.842 | | |
| | 0.95 | 0.923 | | |
| 6 | 0.20 | 0.000 | 0.00 | 1.000 |
| | 0.25 | 0.003 | 0.05 | 0.789 |
| | 0.30 | 0.018 | 0.075 | 0.676 |
| | 0.40 | 0.094 | 0.10 | 0.556 |
| | 0.50 | 0.216 | 0.125 | 0.429 |
| | 0.60 | 0.364 | 0.15 | 0.294 |
| | 0.70 | 0.525 | 0.175 | 0.152 |
| | 0.80 | 0.687 | 0.20 | 0.000 |
| | 0.90 | 0.846 | | |




SYSTEM $PbBr_2$—RbBr

FIG. 4·7 THEORETICAL BREDIG ACTIVITIES

(FLOOD ET AL. ION FRACTIONS)

deviations of the experimental activities of MX from the theoretical activities in the same sense. The difficulty in interpretation here, results from the inaccuracy of the graphical integration in the determination of $a_{MX}$ (experimental). The lower values of the activity of MX for the complex ions $AX_4^{2-}$ and $AX_6^{4-}$, using equivalent ionic fractions, give a greater versatility to this model, in that a greater variety of species are possible. However, the validity of the use of equivalent ion fractions for these systems, as mentioned above, is questionable.

When the activities of both components in the three systems $PbBr_2$-KBr, $PbBr_2$-RbBr and $PbBr_2$-CsBr, are compared with the values calculated using the Bredig equation, the only value for z which is in any way satisfactory, is z = 4. This takes into account the inaccuracies in the determination of $a_{MX}$. Thus, according to this model (using Temkin ion fractions), the complex species contributing greatest to the experimental activity deviations is $PbBr_4^{2-}$.

c) <u>A model based on the assumption of partial dissociation of complex ions</u>

The following method of calculation of the activities of both components of a binary mixture $AX_2$ + MX, is based on the partial dissociation of complex species formed within the melt. In the derivation, it is assumed that:

(i) The alkali metal ion ($M^+$) is not an integral part of the complex;

(ii) The following reactions lie completely to the right:

Excess MX : $N_1AX_2 + N_2MX \rightleftharpoons N_1AX_2^{(z-2)-} + (N_2 - zN_1)X^- + N_2M^+$

Excess $AX_2$ : $N_1AX_2 + N_2MX \rightleftharpoons \frac{1}{(z-2)} N_2AX_z^{(z-2)-} + N_2M^+ + \left[ 2N_1 - \frac{2}{(z-2)}N_2 \right] X^-$

where $N_1$ and $N_2$, are the mole fractions of $AX_2$ and MX respectively and z is the number of $X^-$ ions per $A^{2+}$ ion.

(iii) The complex partially dissociates into $A^{2+}$ and $X^-$ ions, i.e.

$$N_y (1 - \alpha) AX_z^{(z-2)-} \rightleftharpoons (N_y\alpha) A^{2+} + (N_yz\alpha) X^-$$

where $N_y$, is the mole fractinn of the complex ion and $\alpha$, is the degree of dissociation of the complex.

The activities of $AX_2$ (e.g. $PbBr_2$) and MX (e.g. MBr) will be deduced separately, for the formation and partial dissociation of the three complex species $AX_3^-$ ($PbBr_3^-$), $AX_4^{2-}$ ($PbBr_4^{2-}$) and $AX_6^{4-}$ ($PbBr_6^{4-}$).

(i) <u>The complex $PbBr_3^-$ ($PbBr_2$:MBr = 1:1)</u>

Let the following scheme be considered representative of the dissociation of the complex ion:

$$PbBr_3^- \rightleftharpoons Pb^{2+} + 3Br^-$$

Let:- $N_1$ and $N_2$, be the mole fractions of $PbBr_2$ and MBr in the original mixture;

" $n_a$, be the number of gm. ions of species "a";

" $N_a$, be the ion fraction of species "a";

" $a_{MBr}$ and $a_{PbBr_2}$, be given by the Temkin relationships:

$$a_{MBr} = N_{M^+} \cdot N_{Br^-} \cdot \gamma_{MBr}$$

$$= N_{M^+} \cdot N_{Br^-} \qquad (\gamma_{MBr} = 1)$$

$$a_{PbBr_2} = N_{Pb^{2+}} \cdot (N_{Br^-})^2 \qquad (\gamma_{PbBr_2} = 1)$$

There are three cases to consider, namely:

1. The mole fraction of $PbBr_2$ is in excess of that required for the stoichiometric formation of the complex ion.
2. When MBr is in excess.
3. When the mole fraction of $PbBr_2$ is equal to the mole fraction of MBr.

Case 1. $N_1 < N_2$

$$n_{Pb^{2+}} = N_1\alpha$$

$$n_{Br^-} = N_2 - N_1 + 3N_1\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_3^-} = N_1 (1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{M^+} = \frac{N_2}{N_2 + N_1\alpha}$$

$$N_{Br^-} = \frac{N_2 - N_1 + 3N_1\alpha}{N_2 - N_1 + 3N_1\alpha + N_1 - N_1\alpha} = \frac{N_2 + N_1 (3\alpha - 1)}{N_2 + 2N_1\alpha}$$

$$a_{PbBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2} \left[\frac{N_2 + N_1 (3\alpha - 1)}{N_2 + 2N_1\alpha}\right]^2 \qquad (4.36)$$

$$a_{MBr} = \frac{N_2}{N_2 + N_1\alpha} \times \frac{N_2 + N_1 (3\alpha - 1)}{N_2 + 2N_1\alpha} \qquad (4.37)$$

Case 2. $N_1 > N_2$

$$n_{Pb^{2+}} = N_1 - N_2 + N_2\alpha$$

$$n_{Br^-} = 2N_1 - 2N_2 + 3N_2\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_3^-} = N_2 (1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1 - N_2 + N_2\alpha}{N_1 - N_2 + N_2\alpha + N_2} = \frac{N_1 + N_1 (\alpha - 1)}{N_1 + N_2\alpha}$$

$$N_{M^+} = \frac{N_2}{N_1 + N_2\alpha}$$

$$N_{Br^-} = \frac{2N_1 - 2N_2 + 3N_2\alpha}{2N_1 - 2N_2 + 3N_2\alpha + N_2 - N_2\alpha} = \frac{2N_1 + N_2 (3\alpha - 2)}{2N_1 + N_2 (2\alpha - 1)}$$

$$a_{PbBr_2} = \frac{N_1 + N_2 (\alpha - 1)}{N_1 + N_2\alpha} \left[ \frac{2N_1 + N_2 (3\alpha - 2)}{2N_1 + N_2 (2\alpha - 1)} \right]^2 \qquad (4.38)$$

$$a_{MBr} = \frac{N_2}{N_1 + N_2\alpha} \times \frac{2N_1 + N_2 (3\alpha - 2)}{2N_1 + N_2 (2\alpha - 1)} \qquad (4.39)$$

Case 3. $N_1 = N_2$

$$n_{Pb^{2+}} = N_1\alpha$$

$$n_{Br^-} = 3N_1\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_3^-} = N_1 (1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{M^+} = \frac{N_2}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{3N_1\alpha}{3N_1\alpha + N_1 - N_1\alpha} = \frac{3N_1\alpha}{N_1\ (2\alpha - 1)}$$

$$a_{PbBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2}\left[\frac{3\alpha}{2\alpha + 1}\right]^2 \qquad (4.40)$$

$$a_{MBr} = \frac{N_2}{N_1\alpha + N_2} \times \frac{3\alpha}{2\alpha + 1} \qquad (4.41)$$

(ii) The complex $PbBr_4^{2-}$ ($PbBr_2$:MBr = 1:2)

Let the following scheme be considered representative of the dissociation of the complex ion:

$$PbBr_4^{2-} \rightleftharpoons Pb^{2+} + 4Br^-$$

Case 1. $2N_1 < N_2$

$$n_{Pb^{2+}} = N_1\alpha$$

$$n_{Br^-} = N_2 - 2N_1 + 4N_1\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_4^{2-}} = N_1\ (1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{M^+} = \frac{N_2}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{N_2 - 2N_1 + 4N_1\alpha}{N_2 - 2N_1 + 4N_1\alpha + N_1 - N_1\alpha} = \frac{N_2 + 2N_1\ (2\alpha - 1)}{N_2 + N_1\ (3\alpha - 1)}$$

$$a_{PbBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2}\left[\frac{N_2 + 2N_1\ (2\alpha - 1)}{N_2 + N_1\ (3\alpha - 1)}\right]^2 \qquad (4.42)$$

$$a_{MBr} = \frac{N_2}{N_1\alpha + N_2} \times \frac{N_2 + 2N_1\ (2\alpha - 1)}{N_2 + N_1\ (3\alpha - 1)} \qquad (4.43)$$

Case 2. $2N_1 > N_2$

$$n_{Pb^{2+}} = N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha$$

$$n_{Br^-} = 2N_1 - N_2 + 2N_2\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_4^{2-}} = \tfrac{1}{2}N_2\,(1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha}{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha + N_2} = \frac{2N_1 + N_2\,(\alpha + 1)}{2N_1 + N_2\,(\alpha + 1)}$$

$$N_{M^+} = \frac{2N_2}{2N_1 + N_2\,(\alpha + 1)}$$

$$N_{Br^-} = \frac{2N_1 - N_2 + 2N_2\alpha}{2N_1 - N_2 + 2N_2\alpha + \tfrac{1}{2}N_2 - \tfrac{1}{2}N_2\alpha}$$

$$= \frac{4N_1 + 2N_2\,(2\alpha - 1)}{4N_1 + N_2\,(3\alpha - 1)}$$

$$a_{PbBr_2} = \frac{2N_1 + N_2\,(\alpha - 1)}{2N_1 + N_2\,(\alpha + 1)} \left[\frac{4N_1 + 2N_2\,(2\alpha - 1)}{4N_1 + N_2\,(3\alpha - 1)}\right]^2 \qquad (4.44)$$

$$a_{MBr} = \frac{2N_2}{2N_1 + N_2\,(\alpha + 1)} \times \frac{4N_1 + 2N_2\,(2\alpha - 1)}{4N_1 + N_2\,(3\alpha - 1)} \qquad (4.45)$$

Case 3. $2N_1 = N_2$

$$n_{Pb^{2+}} = N_1\alpha$$

$$n_{Br^-} = 4N_1\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_4^{2-}} = N_1\,(1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{M^+} = \frac{N_2}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{4N_1\alpha}{4N_1\alpha + N_1 - N_1\alpha} = \frac{4N_1\alpha}{N_1\ (3\alpha + 1)}$$

$$a_{PbBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2}\left[\frac{4\alpha}{3\alpha + 1}\right]^2 \qquad (4.46)$$

$$a_{MBr} = \frac{N_2}{N_1\alpha + N_2} \times \frac{4\alpha}{3\alpha + 1} \qquad (4.47)$$

(iii) The complex $PbBr_6^{4-}$ ($PbBr_2$:MBr = 1:4)

Let the following scheme be considered representative of the dissociation of the complex ion:

$$PbBr_6^{4-} \rightleftharpoons Pb^{2+} + 6Br^-$$

Case 1. $4N_1 < N_2$

$$n_{Pb^{2+}} = N_1\alpha$$

$$n_{Br^-} = N_2 - 4N_1 + 6N_1\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_6^{4-}} = N_1\ (1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{M^+} = \frac{N_2}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{N_2 - 4N_1 + 6N_1\alpha}{N_2 - 4N_1 + 6N_1\alpha + N_1 - N_1\alpha} = \frac{N_2 + 2N_1\ (3\alpha - 2)}{N_2 + N_1\ (5\alpha - 3)}$$

$$a_{PbBr2} = \frac{N_1\alpha}{N_1\alpha + N_2}\left[\frac{N_2 + 2N_1\ (3\alpha - 2)}{N_2 + N_1\ (5\alpha - 3)}\right]^2 \qquad (4.48)$$

$$a_{MBr} = \frac{N_2}{N_1\alpha + N_2} \times \frac{N_2 + 2N_1\ (3\alpha - 2)}{N_2 + N_1\ (5\alpha - 3)} \qquad (4.49)$$

Case 2. $4N_1 > N_2$

$$n_{Pb^{2+}} = N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha$$

$$n_{Br^-} = 2N_1 - \tfrac{1}{2}N_2 + \tfrac{3}{2}N_2\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_6^{4-}} = \tfrac{1}{2}N_2\ (1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha}{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha + N_2} = \frac{4N_1 + N_2(\alpha - 1)}{4N_1 + N_2\ (\alpha + 3)}$$

$$N_{M^+} = \frac{4N_2}{4N_1 + N_2(\alpha + 3)}$$

$$N_{Br^-} = \frac{2N_1 - \tfrac{1}{2}N_2 + \tfrac{3}{2}N_2\alpha}{2N_1 - \tfrac{1}{2}N_2 + \tfrac{3}{2}N_2\alpha + \tfrac{1}{2}N_2 - \tfrac{1}{2}N_2\alpha}$$

$$= \frac{8N_1 + 2N_2\ (3\alpha - 1)}{8N_1 + N_2\ (5\alpha - 1)}$$

$$a_{PbBr_2} = \frac{4N_1 + N_2\ (\alpha - 1)}{4N_1 + N_2\ (\alpha + 3)} \left[\frac{8N_1 + 2N_2\ (3\alpha - 1)}{8N_1 + N_2\ (5\alpha - 1)}\right]^2 \qquad (4.50)$$

$$a_{MBr} = \frac{4N_2}{4N_1 + N_2\ (\alpha + 3)} \times \frac{8N_1 + 2N_2\ (3\alpha - 1)}{8N_1 + N_2\ (5\alpha - 1)} \qquad (4.51)$$

Case 3. $4N_1 = N_2$

$$n_{Pb^{2+}} = N_1\alpha$$

$$n_{Br^-} = 6N_1\alpha$$

$$n_{M^+} = N_2$$

$$n_{PbBr_6^{4-}} = N_1\ (1 - \alpha)$$

$$N_{Pb^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{M^+} = \frac{N_2}{N_2 + N_1\alpha}$$

$$N_{Br^-} = \frac{6N_1\alpha}{6N_1\alpha + N_1 - N_1\alpha} = \frac{6N_1\alpha}{N_1\,(5\alpha + 1)}$$

$$a_{PbBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2}\left[\frac{6\alpha}{5\alpha + 1}\right]^2 \qquad (4.52)$$

$$a_{MBr} = \frac{N_2}{N_1\alpha + N_2} \times \frac{6\alpha}{5\alpha + 1} \qquad (4.53)$$

(iv) Calculation of dissociation constants

The complex $PbBr_3^-$

$$PbBr_3^- \rightleftharpoons Pb^{2+} + 3Br^-$$

No. moles at equilibrium = $(1-\alpha)$ $\alpha$ $3\alpha$

Total no.moles = $(1 + 3\alpha)$

$$K = \frac{[Pb^{2+}][Br^-]^3}{[PbBr_3^-]}$$

$$= \frac{\frac{\alpha}{1 + 3\alpha}\left[\frac{3\alpha}{1 + 3\alpha}\right]^3}{\frac{1 - \alpha}{1 + 3\alpha}}$$

$$= \frac{27\alpha^4}{(1-\alpha)(1 + 3\alpha)^3} \qquad (4.54)$$

The complex $PbBr_4^{2-}$

$$PbBr_4^{2-} \rightleftharpoons Pb^{2+} + 4Br^-$$

No. moles at equilibrium = $(1-\alpha)$ $\alpha$ $4\alpha$

Total no. of moles = $(1 + 4\alpha)$

$$K = \frac{[Pb^{2+}][Br^-]^4}{[PbBr_4^{2-}]}$$

$$= \frac{\frac{\alpha}{1+4\alpha}\left[\frac{4\alpha}{1+4\alpha}\right]^4}{\frac{1-\alpha}{1+4\alpha}}$$

$$= \frac{256\alpha^5}{(1-\alpha)(1+4\alpha)^4} \qquad (4.55)$$

The complex $PbBr_6^{4-}$

$$PbBr_6^{4-} \rightleftharpoons Pb^{2+} + 6Br^-$$

No. moles at equilibrium = $(1-\alpha)$ $\alpha$ $6\alpha$

Total no. of moles = $(1 + 6\alpha)$

$$K = \frac{[Pb^{2+}][Br^-]^6}{[PbBr_6^{4-}]}$$

$$= \frac{\frac{\alpha}{1+6\alpha}\left[\frac{6\alpha}{1+6\alpha}\right]^6}{\frac{1-\alpha}{1+6\alpha}}$$

$$= \frac{4.669 \times 10^4\alpha^7}{(1-\alpha)(1+6\alpha)^6} \qquad (4.56)$$

The values for $\alpha$ have been calculated from eqns. 4.40, 4.46 and 4.52, by a trial and error procedure, having assumed the value for $a_{PbBr_2}$ as read from the plots of the activity of $PbBr_2$ versus composition for each of the three alkali halide mixtures. The activity reference point for $\alpha$ was taken as the composition corresponding to the stoichiometry of the complex ion. To calculate the activity of lead bromide, the value for $\alpha$, for a particular complex ion in each system, was inserted in the corresponding equation. The dissociation constants for the complex ions $PbBr_z^{(z-2)-}$, were calculated for each system using eqns. 4.54-4.56. The theoretical values for $\alpha$, K (dissoc.) and $a_{PbBr_2}$, are found in Tables 4.12-4.14 and the activities are represented diagrammatically in figs. 4.8-4.10.

In the Bredig method of theoretically estimating the activities, the only ions of $M^+$, $Pb^{2+}$ and $Br^-$, which contribute to the ion fractions, are those in excess of that required for the stoichiometry of the complex. For this method, although $M^+$ ions are unaffected by complex formation (being independent of partial dissociation of the species), the numbers of $Pb^{2+}$ and $Br^-$ ions are increased (to an extent dependent on $\alpha$) as a result of incomplete stability of the complex ions. The activity of $PbBr_2$ will therefore lie between the two extremes of the ideal Temkin activity ($\alpha = 1$) and the activity calculated from infinite complex stability ($\alpha = 0$). The activity of MBr need not, and in fact does not, fall within these same limits. Only for a limited range of values for $\alpha$ (see Table 4.15) does the theoretical activity of MBr fall between that of Bredig and Temkin.

TABLE 4.12

The system $PbBr_2$-KBr
Comparison of theoretical and experimental activities of $PbBr_2$, assuming partial dissociation of complex ions

| complex ion and relative data | mole fraction $PbBr_2$ | a(theoretical) | a(exptl.) (600°C) |
|---|---|---|---|
| $PbBr_3^-$ | 0.10 | 0.062 | 0.027 |
| Ref. pt. : $N_1 = 0.5$ | 0.20 | 0.120 | 0.046 |
| $a_1 = 0.277$ | 0.30 | 0.175 | 0.072 |
| $\alpha = 0.64$ | 0.40 | 0.227 | 0.123 |
| $K = 5.05 \times 10^{-1}$ | 0.50 | 0.277 | 0.274 |
| | 0.60 | 0.422 | 0.517 |
| | 0.70 | 0.571 | 0.655 |
| | 0.80 | 0.718 | 0.770 |
| | 0.90 | 0.861 | 0.884 |
| $PbBr_4^{2-}$ | 0.10 | 0.035 | 0.027 |
| Ref. pt. : $N_1 = 0.33$ | 0.20 | 0.063 | 0.046 |
| $a_1 = 0.084$ | 0.30 | 0.079 | 0.072 |
| $\alpha = 0.38$ | 0.33 | 0.080 | 0.084 |
| $K = 8.12 \times 10^{-2}$ | 0.40 | 0.160 | 0.123 |
| | 0.50 | 0.295 | 0.274 |
| | 0.60 | 0.439 | 0.517 |
| | 0.70 | 0.584 | 0.655 |
| | 0.80 | 0.727 | 0.770 |
| | 0.90 | 0.866 | 0.884 |
| $PbBr_6^{4-}$ | 0.10 | 0.030 | 0.027 |
| Ref. pt. : $N_1 = 0.20$ | 0.20 | 0.045 | 0.046 |
| $a_1 = 0.045$ | 0.30 | 0.147 | 0.072 |
| $\alpha = 0.34$ | 0.40 | 0.265 | 0.123 |
| $K = 4.71 \times 10^{-2}$ | 0.50 | 0.387 | 0.274 |
| | 0.60 | 0.514 | 0.517 |

Table 4.12 (contd.)

| complex ion and relative data | mole fraction $PbBr_2$ | a(theoretical) | a(exptl.) (600°C) |
|---|---|---|---|
| $PbBr_6^{4-}$ (contd.) | 0.70 | 0.639 | 0.655 |
| | 0.80 | 0.761 | 0.770 |
| | 0.90 | 0.882 | 0.884 |

TABLE 4.13

The system $PbBr_2$-RbBr
Comparison of experimental and theoretical activities of $PbBr_2$, assuming partial dissociation of complex ions

| complex ion and relative data | mole fraction $PbBr_2$ | a(theoretical) | a(exptl.) (600°C) |
|---|---|---|---|
| $PbBr_3^-$ | 0.10 | 0.051 | 0.005 |
| Ref. pt. : $N_1 = 0.5$ | 0.20 | 0.096 | 0.020 |
| $a_1 = 0.206$ | 0.30 | 0.137 | 0.046 |
| $\alpha = 0.53$ | 0.40 | 0.174 | 0.100 |
| $K = 2.61 \times 10^{-1}$ | 0.50 | 0.206 | 0.205 |
| | 0.60 | 0.363 | 0.380 |
| | 0.70 | 0.528 | 0.579 |
| | 0.80 | 0.691 | 0.749 |
| | 0.90 | 0.849 | 0.892 |
| $PbBr_4^{2-}$ | 0.10 | 0.030 | 0.005 |
| Ref. pt. : $N_1 = 0.33$ | 0.20 | 0.051 | 0.020 |
| $a_1 = 0.060$ | 0.30 | 0.061 | 0.046 |
| $\alpha = 0.323$ | 0.33 | 0.060 | 0.060 |
| $K = 4.82 \times 10^{-2}$ | 0.40 | 0.136 | 0.100 |
| | 0.50 | 0.274 | 0.205 |
| | 0.60 | 0.422 | 0.380 |
| | 0.70 | 0.573 | 0.579 |
| | 0.80 | 0.715 | 0.749 |
| | 0.90 | 0.863 | 0.892 |

Table 4.13 (contd.)

| complex ion and relative data | mole fraction $PbBr_2$ | a(theoretical) | a(exptl.) (600°C) |
|---|---|---|---|
| $PbBr_6^{4-}$ | 0.10 | 0.021 | 0.005 |
| Ref. pt. : $N_1$ = 0.2 | 0.20 | 0.025 | 0.020 |
| $a_1$ = 0.025 | 0.30 | 0.120 | 0.046 |
| $\alpha$ = 0.24 | 0.40 | 0.240 | 0.100 |
| K = $1.33 \times 10^{-2}$ | 0.50 | 0.368 | 0.205 |
| | 0.60 | 0.499 | 0.380 |
| | 0.70 | 0.628 | 0.579 |
| | 0.80 | 0.755 | 0.749 |
| | 0.90 | 0.879 | 0.892 |

TABLE 4.14

The system $PbBr_2$-CsBr
Comparison of experimental and theoretical activities of $PbBr_2$, assuming partial dissociation of complex ions

| complex ion and relative data | mole fraction $PbBr_2$ | a(theoretical) | a(exptl.) (600°C) |
|---|---|---|---|
| $PbBr_3^-$ | 0.10 | 0.054 | 0.001 |
| Ref. pt. : $N_1$ = 0.5 | 0.20 | 0.103 | 0.011 |
| $a_1$ = 0.224 | 0.30 | 0.147 | 0.033 |
| $\alpha$ = 0.56 | 0.40 | 0.188 | 0.088 |
| K = $3.14 \times 10^{-1}$ | 0.50 | 0.224 | 0.224 |
| | 0.60 | 0.380 | 0.387 |
| | 0.70 | 0.540 | 0.570 |
| | 0.80 | 0.698 | 0.796 |
| | 0.90 | 0.852 | 0.947 |
| $PbBr_4^{2-}$ | 0.10 | 0.026 | 0.001 |
| Ref. pt. : $N_1$ = 0.33 | 0.20 | 0.043 | 0.011 |
| $a_1$ = 0.045 | 0.30 | 0.048 | 0.033 |
| $\alpha$ = 0.28 | 0.33 | 0.045 | 0.043 |
| K = $3.03 \times 10^{-2}$ | 0.40 | 0.123 | 0.088 |

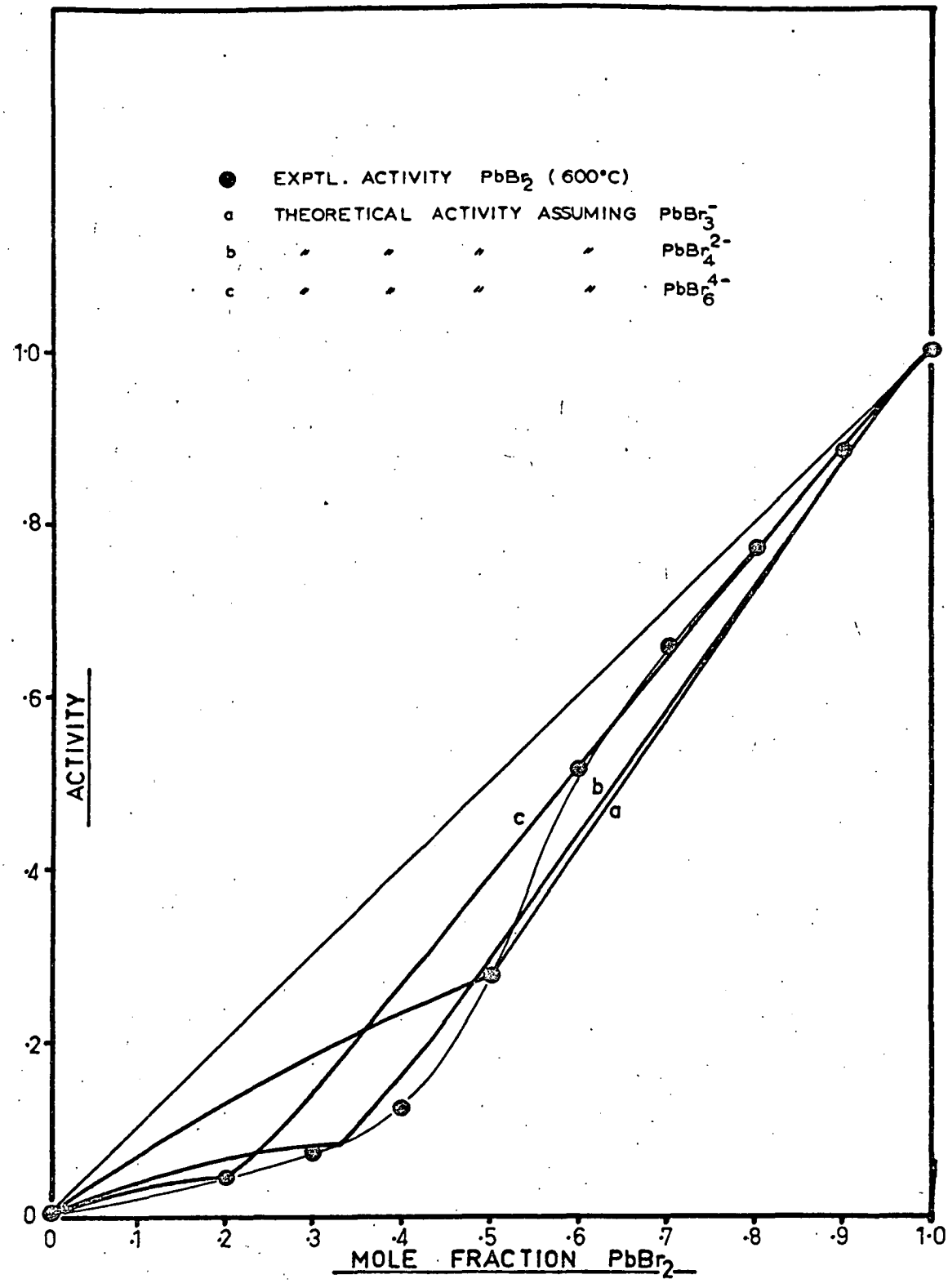
Table 4.14 (contd.)

| complex ion and relative data | mole fraction $PbBr_2$ | a(theoretical) | a(exptl.) (600°C) |
|---|---|---|---|
| $PbBr_4^{2-}$ (contd.) | 0.50 | 0.258 | 0.224 |
| | 0.60 | 0.409 | 0.387 |
| | 0.70 | 0.564 | 0.570 |
| | 0.80 | 0.715 | 0.796 |
| | 0.90 | 0.861 | 0.947 |
| $PbBr_6^{4-}$ | 0.10 | 0.018 | 0.001 |
| Ref. pt. : $N_1 = 0.2$ | 0.20 | 0.012 | 0.011 |
| $a_1 = 0.012$ | 0.30 | 0.101 | 0.033 |
| $\alpha = 0.17$ | 0.40 | 0.222 | 0.088 |
| $K = 3.39 \times 10^{-3}$ | 0.50 | 0.354 | 0.224 |
| | 0.60 | 0.487 | 0.387 |
| | 0.70 | 0.620 | 0.570 |
| | 0.80 | 0.751 | 0.796 |
| | 0.90 | 0.877 | 0.947 |

TABLE 4.15

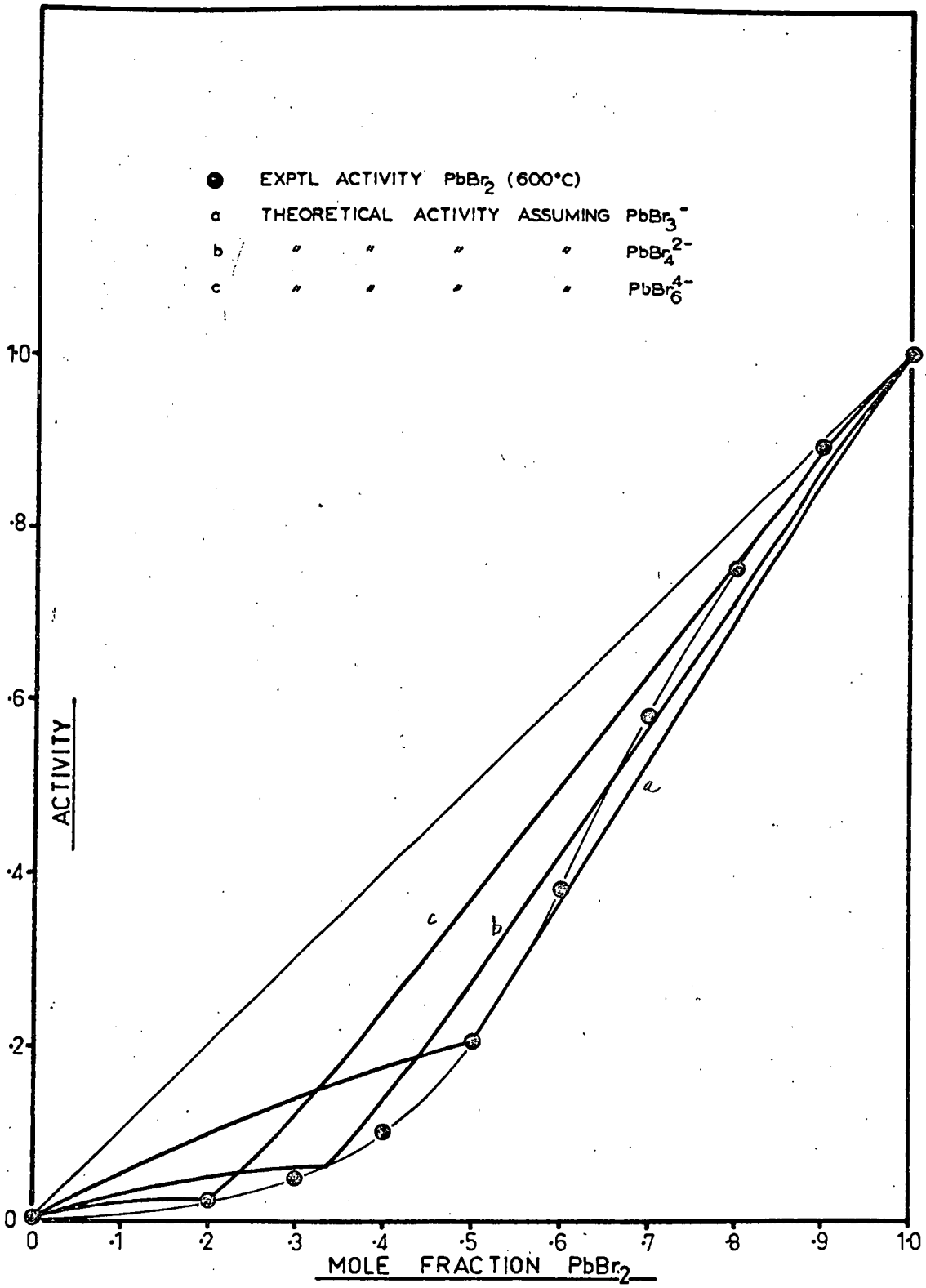
Range in values for the degree of dissociation of complexes producing activities of MBr which lie between the Temkin and Bredig values

| complex ion | composition range | values for $\alpha$ for which $a_{MBr}$ > Bredig < Temkin |
|---|---|---|
| $PbBr_3^-$ | $N_1 < N_2$ | 0 - 0.5 |
| | $N_1 > N_2$ | 0 - $(2N_2 - N_1)/2N_2$ |
| $PbBr_4^{2-}$ | $2N_1 < N_2$ | 0 - 0.667 |
| | $2N_1 > N_2$ | 0 - $(3N_2 - 2N_1)/3N2$ |
| $PbBr_6^{4-}$ | $4N_1 < N_2$ | 0 - 0.8 |
| | $4N_1 > N_2$ | 0 - $(5N_2 - 4N_1)/5N_2$ |




SYSTEM $PbBr_2$—KBr

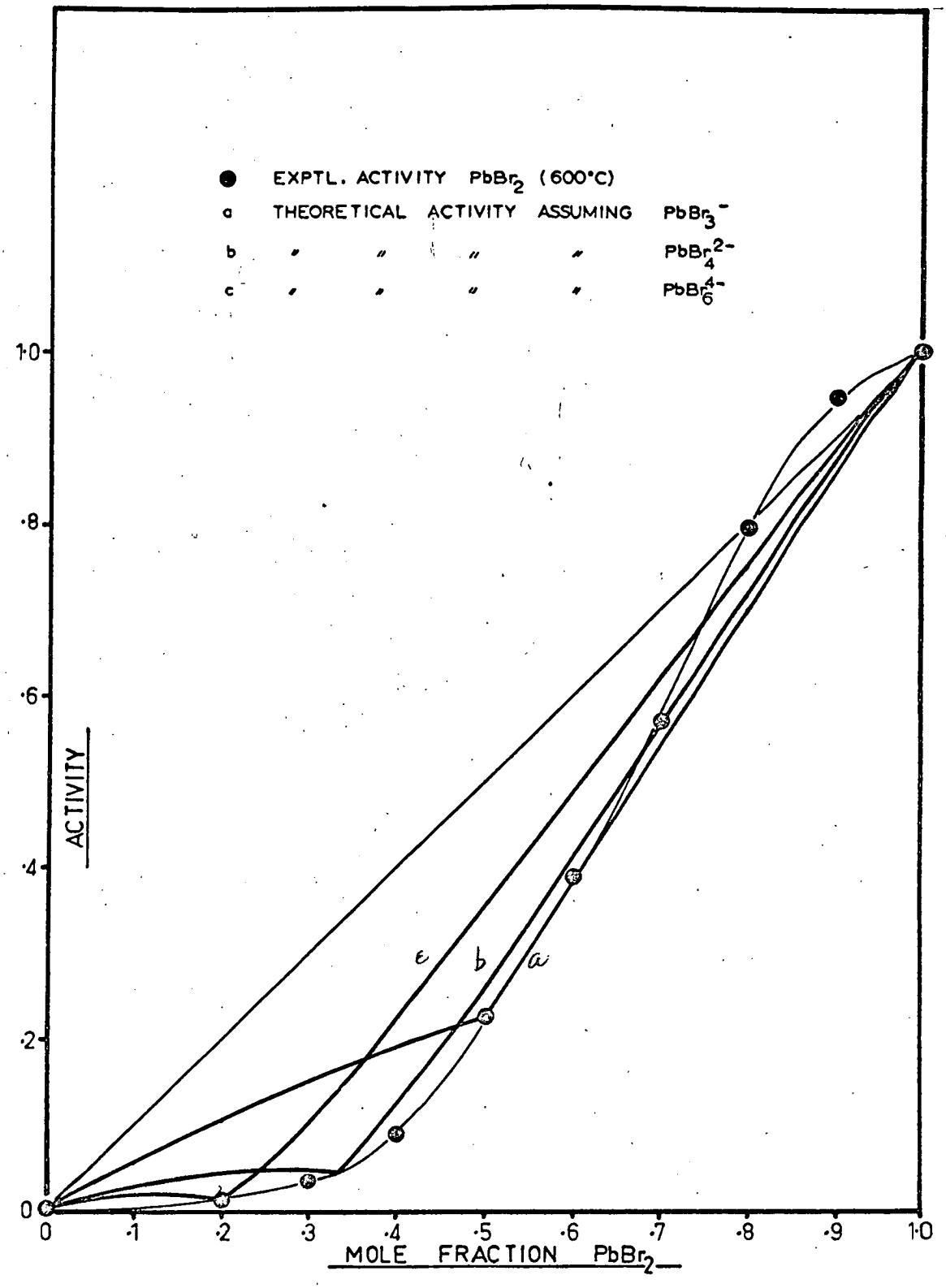
FIG. 4·8 THEORETICAL ACTIVITIES FOR $PbBr_2$ ASSUMING PARTIAL DISSN. OF CPLX. IONS




SYSTEM $PbBr_2$–RbBr

FIG. 4·9

THEORETICAL ACTIVITIES FOR $PbBr_2$ ASSUMING PARTIAL DISSN. OF CPLX. IONS




SYSTEM $PbBr_2$—CsBr

FIG. 4·10 THEORETICAL ACTIVITIES FOR $PbBr_2$ ASSUMING PARTIAL DISSN. OF CPLX. IONS

Other values produce small positive deviations from the ideal Temkin activity over the corresponding range of composition. This occurs because of the reciprocal dependence of $N_{M^+}$ on $\alpha$; as $\alpha$ decreases, then, $N_{M^+}$ increases, $N_{Pb^{2+}}$ decreases and $N_{Br^-}$ decreases (the rate of decrease of $N_{Br^-}$ is fast when for $N_1 < N_2$, $\alpha < 0.5$ and for $N_1 > N_2$, $\alpha < (2N_2 - N_1)/2N_2$ for the complex ion $PbBr_3^-$ etc.). For the species $PbBr_3^-$, $N_{M^+}$ increases faster than $N_{Br^-}$ decreases, for values of $\alpha$ between 0.5-1.0 when $N_2 > N_1$, and $(2N_2 - N_1)/2N_2$-1.0 when $N_2 < N_1$. This results in an increase in the theoretical activity of MBr above that of the Temkin activity. Similar phenomena occur for the other complex ions. This model is therefore considered inadequate for deriving the activity of the alkali halide component.

It is obvious, from a comparison of the theoretical with the experimental activities and also from figs. 4.8-4.10, that on the basis of this model, the postulate of the presence of a single complex ion is insufficient to explain the behaviour of each system over the whole composition range. Nevertheless, it is more realistic than the model of Bredig, in that by postulating a dissociation scheme for each complex ion, the calculated activity curve for $PbBr_2$ approximates more closely that calculated from the experimental data.

d) <u>A model based on the assumption of stepwise complex formation</u>

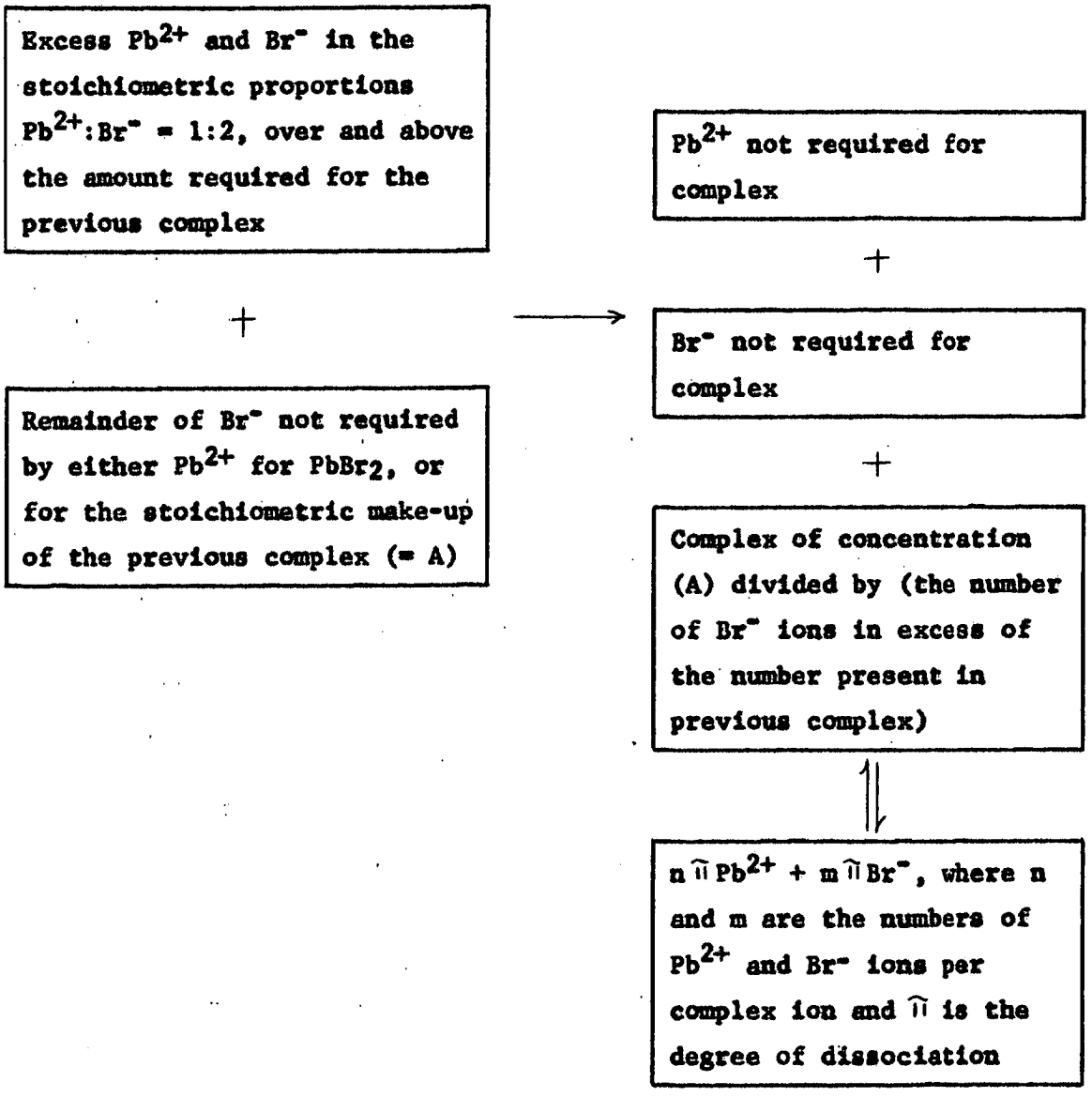
It was found that the activity model for partial complex ion dissociation was applicable only for small composition ranges in the vicinity of the stoichiometric composition of the associated species.

On the basis of a continuous complex formation hypothesis, it seems plausible that a series of dissociation steps may be formulated, e.g., commencing with the ion $PbBr_3^-$ and terminating with the ion $PbBr_6^{4-}$. Each species will have its own dissociation constant and hence contribute to the overall activity of $PbBr_2$ to different extents. The resultant plot of $a_{PbBr_2}$ versus composition, will therefore be representative of the sum of the interactions for each complex species present at that composition. Further, it will be assumed that for each composition, the melt may be considered to consist of many complex species in equilibrium.

Owing to the analogy of this scheme to that of partial complex dissociation, the inapplicability of this model to the calculation of $a_{MBr}$, unfortunately still holds. For simplicity, the following derivation will be concerned only with the three complex ions $PbBr_3^-$, $PbBr_4^{2-}$ and $PbBr_6^{4-}$, having degrees of dissociation $\alpha$, $\beta$ and $\gamma$, respectively. Only the case where excess $PbBr_2$ is present above that required for quantitative complex formation will be considered. The scheme is based on the reaction on page 250.

Consider a mixture of $PbBr_2$ and MBr, of mole fractions $N_1$ and $N_2$, respectively. Let the symbols have the same significance as in the previous model.

## Model pertaining to stepwise complex ion formation



$$(N_1)PbBr_2 + (N_2)Br^-$$

$$\downarrow$$

$$(3N_2\alpha)Br^- + (N_2\alpha)Pb^{2+} \rightleftharpoons (N_2)PbBr_3^- + (N_1 - N_2)Pb^{2+} + (2N_1 - 2N_2)Br^-$$

Total $Pb^{2+} = N_1 - N_2 + N_2\alpha$

Amt. $Br^-$ for stoichiometric $PbBr_2$

$= 2(N_1 - N_2 + N_2\alpha)$

Remainder of $Br^-$

$= 2N_1 - 2N_2 + 3N_2\alpha - 2N_1 + 2N_2 - 2N_2\alpha$

$= N_2\alpha$

$$\downarrow$$

$$(\tfrac{1}{2}N_2\alpha\beta)Pb^{2+} + (2N_2\alpha\beta)Br^- \rightleftharpoons (\tfrac{1}{2}N_2\alpha)PbBr_4^{2-} + (N_1 - N_2 + \tfrac{1}{2}N_2\alpha)Pb^{2+} + (2N_1 - 2N_2 + N_2\alpha)Br^-$$

Total $Pb^{2+} = N_1 - N_2 + \tfrac{1}{2}N_2\alpha + \tfrac{1}{2}N_2\alpha\beta$

Amt. $Br^-$ for stoichiometric $PbBr_2$

$= 2(N_1 - N_2 + \tfrac{1}{2}N_2\alpha + \tfrac{1}{2}N_2\alpha\beta)$

Remainder of $Br^-$

$= 2N_1 - 2N_2 + N_2\alpha + 2N_2\alpha\beta$

$- 2N_1 + 2N_2 - N_2\alpha - N_2\alpha\beta$

$= N_2\alpha\beta$

$$\downarrow$$

$$(\tfrac{1}{2}N_2\alpha\beta\gamma)Pb^{2+} + (3/2N_2\alpha\beta\gamma)Br^- \rightleftharpoons (\tfrac{1}{2}N_2\alpha\beta)PbBr_6^{4-} + (N_1 - N_2 + \tfrac{1}{2}N_2\alpha + \tfrac{1}{2}N_2\alpha\beta)Pb^{2+} + (2N_1 - 2N_2 + N_2\alpha + \tfrac{1}{2}N_2\alpha\beta)Br^-$$

(contd. on p.252)

$$\text{Total } Pb^{2+} = N_1 - N_2 + \tfrac{1}{2}N_2\alpha + \tfrac{1}{2}N_2\alpha\beta + \tfrac{1}{2}N_2\alpha\beta\gamma$$

$$= N_1 + N_2\,(\tfrac{1}{2}\alpha + \tfrac{1}{2}\alpha\beta + \tfrac{1}{2}\alpha\beta\gamma - 1)$$

$$\text{Total } Br^- = 2N_1 - 2N_2 + N_2\alpha + \tfrac{1}{2}N_2\alpha\beta + 3/2\,\alpha\beta\gamma$$

$$= 2N_1 + N_2\,(\alpha + \tfrac{1}{2}\alpha\beta + 3/2\,\alpha\beta\gamma - 2)$$

$$\text{Total } M^+ = N_2$$

$$\text{Total complex} = N_2(1-\alpha) + \tfrac{1}{2}N_2\alpha(1-\beta) + \tfrac{1}{2}N_2\alpha\beta(1-\gamma)$$

$$= N_2 - N_2\alpha + \tfrac{1}{2}N_2\alpha - \tfrac{1}{2}N_2\alpha\beta + \tfrac{1}{2}N_2\alpha\beta - \tfrac{1}{2}N_2\alpha\beta\gamma$$

$$= N_2(1 - \tfrac{1}{2}\alpha - \tfrac{1}{2}\alpha\beta - \tfrac{1}{2}\alpha\beta\gamma)$$

$$N_{Pb^{2+}} = \frac{4N_1 + N_2(2\alpha + \alpha\beta + \alpha\beta\gamma - 4)}{4N_1 + N_2(2\alpha + \alpha\beta + \alpha\beta\gamma)}$$

$$N_{Br^-} = \frac{2N_1 + N_2(\alpha + \tfrac{1}{2}\alpha\beta + 3/2\,\alpha\beta\gamma - 2)}{2N_1 + N_2(\alpha + \tfrac{1}{2}\alpha\beta + 3/2\,\alpha\beta\gamma - 2 + 1 - \tfrac{1}{2}\alpha - \tfrac{1}{2}\alpha\beta - \tfrac{1}{2}\alpha\beta\gamma)}$$

$$= \frac{8N_1 + 2N_2(2\alpha + \alpha\beta + 3\alpha\beta\gamma - 4)}{8N_1 + N_2(2\alpha + \alpha\beta + 5\alpha\beta\gamma - 4)}$$

$$a_{PbBr_2} = N_{Pb^{2+}} \cdot (N_{Br^-})^2 \qquad (\text{assume } \gamma_{PbBr_2} = 1)$$

$$= \frac{4N_1 + N_2(2\alpha + \alpha\beta + \alpha\beta\gamma - 4)}{4N_1 + N_2(2\alpha + \alpha\beta + \alpha\beta\gamma)} \times \left[\frac{8N_1 + 2N_2(2\alpha + \alpha\beta + 3\alpha\beta\gamma - 4)}{8N_1 + N_2(2\alpha + \alpha\beta + 5\alpha\beta\gamma - 4)}\right]^2 \qquad (4.57)$$

The final expression for the activity of $PbBr_2$ (eqn. 4.57) involves three independent dissociation constants and is of such a nature as to be insoluble in terms of $a_{PbBr_2}$ by the method of trial and error. Time did not permit a more detailed analysis, other than a trial substitution of a random set of values for $\alpha$, $\beta$ and $\gamma$ and observation of the shape of the activity-composition curve. Such a substitution was carried out with $\alpha$, $\beta$ and $\gamma$, respectively equal to

0.8, 0.6 and 0.5. The results are presented in Table 4.16 and fig. 4.11, together with the 600°C isotherm for the system $PbBr_2$-RbBr to serve as a comparison. Although this does not exactly reproduce the experimental activity isotherms, it does illustrate the potential of such a model.

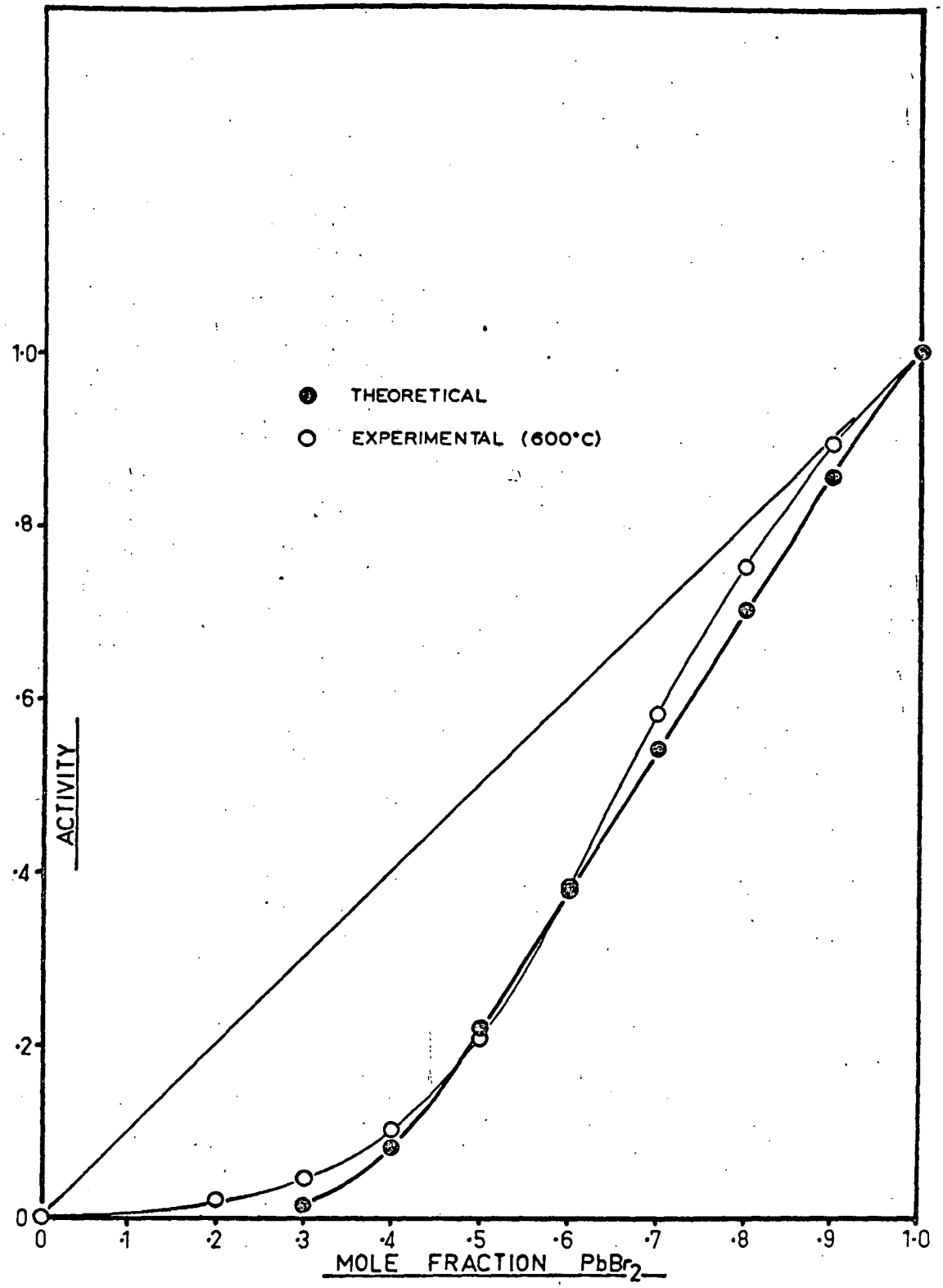
TABLE 4.16

Trial calculation of the activity of $PbBr_2$ for stepwise complex formation with $\alpha = 0.8, \beta = 0.6, \gamma = 0.5$

| mole fraction $PbBr_2$ ($N_1$) | mole fraction MBr ($N_2$) | $a_{PbBr_2}$ (calc.) | $a_{PbBr_2}$ (exptl.) System $PbBr_2$-RbBr (600°C) |
|---|---|---|---|
| 0.30 | 0.70 | 0.012 | 0.046 |
| 0.40 | 0.60 | 0.080 | 0.100 |
| 0.50 | 0.50 | 0.217 | 0.205 |
| 0.60 | 0.40 | 0.376 | 0.380 |
| 0.70 | 0.30 | 0.539 | 0.579 |
| 0.80 | 0.20 | 0.700 | 0.749 |
| 0.90 | 0.10 | 0.854 | 0.892 |
| 1.00 | 0.00 | 1.000 | 1.000 |

e) Comparison of the activity models

None of the four models discussed, defines the experimental activity of lead bromide exactly. The closest approach is obtained with the Hildebrand model and potentially also, the model based on the assumption of stepwise formation of complexes. The former is capable of explaining the positive deviation of $a_{PbBr_2}$ from the Temkin value, in the system $PbBr_2$-CsBr. In order to explain this




SYSTEM $PbBr_2$—RbBr

FIG. 4·11 STEP-WISE COMPLEX FORMN. MODEL FOR ACTIVITY $PbBr_2$ COMPARED TO EXPTL. RESULTS

deviation using the latter model, further dissociation schemes are necessary which are applicable to solutions containing 80-100 mole % $PbBr_2$ and involving an equilibrium between $PbBr_2$, $Pb^{2+}$ and $Br^-$. Although the Bredig and partial complex dissociation models give poor agreement with the experimental activity of $PbBr_2$, they are valuable in indicating the species present in the mixtures. This is also true for the Bredig model, with reference to the activity of MBr, although, in this case, the error in the experimental value for $a_{MBr}$ prevents any accurate qualitative comparison. None of the models proposed is capable of estimating the activity of the alkali halide component.

That there is more than one species in the molten mixtures is suggested by all the models, with perhaps the exception of the Hildebrand model as applied to the system $PbBr_2$-RbBr, where agreement between theory and experiment for the ion $PbBr_3^-$ is extremely good. The need for postulating more than one complex, is especially necessary in the case of activities calculated on the basis of a stepwise formation of complexes. The dissociation constants of the three complex ions, $PbBr_3^-$, $PbBr_4^{2-}$ and $PbBr_6^{4-}$, as calculated from the Hildebrand and partial complex dissociation models, show a similar trend, in so far as their magnitudes and their gradation through the series KBr - RbBr - CsBr are concerned. (The dissociation constants for the complexes calculated from the Hildebrand model are given by the reciprocal of the association constants.) The two sets of values are summarized in Table 4.17. The dissociation constants indicate two trends. Firstly, the stability of the complex ion increases with

TABLE 4.17

Comparison of the dissociation constants of the complex ions $PbBr_3^-$, $PbBr_4^{2-}$, $PbBr_6^{4-}$ calculated from the Hildebrand and Partial Dissociation models

| complex ion | System | Hildebrand model | | Part. dissoc. |
|---|---|---|---|---|
| | | K assoc. | K dissoc. | K dissoc. |
| $PbBr_3^-$ | $PbBr_2$-KBr | 6.02 | $1.66 \times 10^{-1}$ | $5.05 \times 10^{-1}$ |
| | $PbBr_2$-RbBr | 13.81 | $0.72 \times 10^{-1}$ | $2.61 \times 10^{-1}$ |
| | $PbBr_2$-CsBr | 11.12 | $0.90 \times 10^{-1}$ | $3.14 \times 10^{-1}$ |
| $PbBr_4^{2-}$ | $PbBr_2$-KBr | 23.00 | $4.35 \times 10^{-2}$ | $8.12 \times 10^{-2}$ |
| | $PbBr_2$-RbBr | 42.90 | $2.33 \times 10^{-2}$ | $4.82 \times 10^{-2}$ |
| | $PbBr_2$-CsBr | 80.40 | $1.24 \times 10^{-2}$ | $3.03 \times 10^{-2}$ |
| $PbBr_6^{4-}$ | $PbBr_2$-KBr | | | $4.71 \times 10^{-2}$ |
| | $PbBr_2$-RbBr | | | $1.33 \times 10^{-2}$ |
| | $PbBr_2$-CsBr | | | $3.39 \times 10^{-3}$ |

increasing co-ordination number. This, however, assumes that each complex ion is alone responsible for the decreased activity of $PbBr_2$ at the composition corresponding to the stoichiometry of the compound, which is not in accordance with the assumed theory of stepwise complex formation. Secondly, the stabilities of the complex ions increase with increasing ionic radius of the alkali metal ion, except for an inversion of order in the case of $PbBr_3^-$ for the systems $PbBr_2$-RbBr and $PbBr_2$-CsBr. However, the actual magnitudes of the dissociation constants are questionable (although these conclusions have been reached in a previous section), on account of the influence of other complex

ions within the melt*. Consider the mixture corresponding to the stoichiometric composition of the complex ion $PbBr_6^{4-}$, i.e. 20 mole % $PbBr_2$ and 80 mole % MBr. If in this mixture it is assumed that the three complex ions $PbBr_3^-$, $PbBr_4^{2-}$ and $PbBr_6^{4-}$ exist in equilibrium, then the deviation of $a_{PbBr_2}$ from the Temkin activity will be due to all these species. Thus, the contribution due to $PbBr_6^{4-}$ may only constitute a small proportion of this and the magnitude of K (dissoc.) for this ion would therefore be much less than the quoted value. Any heat of mixing of like ions will also have an effect on the deviations of the experimental activity from the Temkin value (see Section 4A.1) and this will affect the value of K.

---

* The value of K in the partial dissociation of complexes scheme is calculated at mole fractions, $N_1$ = 0.2, 0.33, 0.5, for the complex ions $PbBr_6^{4-}$, $PbBr_4^{2-}$ and $PbBr_3^-$, respectively and it is assumed that at each of these reference points the corresponding complex ion is the only one present.

## SECTION B

## THE THREE COMPONENT SYSTEMS

## $PbCl_2$-CsCl-MCl

## (WHERE M = Li, Na, K, Rb, Cs)

## 4B.1 THE BINARY SYSTEM $PbCl_2$-CsCl (i.e. M = Cs)

### a) Activity of the components

As in the case of the binary lead bromide systems, it will be assumed that in the standard state (the pure salt), $PbCl_2$ is associated to a certain extent (e.g. as $PbCl_2$ molecules).

The deviations of the 700°C activity isotherm from the ideal Temkin curve in this system (see Table 4.18, fig. 3.23), show a marked similarity to those of the 600°C isotherm for the system $PbBr_2$-CsBr. The main difference is the point of inflection in the

TABLE 4.18

System $PbCl_2$-CsCl
Deviation of the 700°C activity isotherm for $PbCl_2$ from the ideal Temkin value

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| m.f. $PbCl_2$ | 0.20 | 0.25 | 0.30 | 0.35 | 0.40 | 0.45 | 0.50 | 0.55 |
| $-\Delta a_{PbCl_2}$ (%) | 95 | 92 | 90 | 86 | 80 | 71 | 61 | 51 |
| m.f. $PbCl_2$ | 0.60 | 0.65 | 0.70 | 0.75 | 0.80 | 0.85 | 0.90 | 0.95 |
| $-\Delta a_{PbCl_2}$ (%) | 40 | 29 | 17 | 12 | 13 | 14 | 0 | -1 |

$a_{PbCl_2}$ veraus composition curve in the range 80-85 mole % $PbCl_2$. The errors in this region have been discussed in Section 3.2b. The deviations of $a_{PbCl_2}$ from the Temkin activity for compositions 80-85 mole % $PbCl_2$, could be explained by the formation of complex ions such as $Pb_4Cl_9^-$. However, the magnitude of the errors in the determination of the activity of $PbCl_2$ for these compositions, together with the

unlikelihood of this species so far (200°C) from the melting point of the mixture (see Section 4A.2a), make such an explanation inadequate.

The smaller magnitude of the positive deviation of $a_{PbCl_2}$ in the system $PbCl_2$-CsCl (compared to $a_{PbBr_2}$ in the system $PbBr_2$-CsBr) and the smaller composition range over which this occurs (90-100 mole % $PbCl_2$ compared to 80-100 mole % $PbBr_2$), can be explained in either of two ways. The tendency to form complex species may be greater than that for the dissociation of $PbCl_2$ "molecules", or alternatively, complexing plays no major role in this composition region and molten $PbCl_2$ is less associated than molten $PbBr_2$ in the first place. The latter explanation seems more probable.

Since the activity coefficient isotherms of $PbBr_2$ and $PbCl_2$ for the systems involving CsBr and CsCl respectively, are so similar for the compositions rich in alkali halide, they may be interpreted in the same way. The absence of a minimum in $\gamma_{PbCl_2}$ and the tendency for the estimated values of $\Delta a_{PbCl_2}$ to become constant between 20 and 30 mole % $PbCl_2$, suggests that the most predominant complex species may be $PbCl_6^{4-}$.

In the composition region between 30 and 70 mole % $PbCl_2$, a slight increase in the activity of $PbCl_2$ with temperature is noted. Nowhere within these composition limits is the increase greater than 0.005 units - a value noticeably less than that for the system $PbBr_2$-RbBr. The reverse temperature dependence of $a_{PbBr_2}$ is observed for the system $PbBr_2$-CsBr. This suggests that the polarization of the

Pb — Cl "bonds" of the chloro complexes by $Cs^+$ is intermediate between the polarization of the Pb — Br "bonds" of the bromo complexes by $Rb^+$ and $Cs^+$. Thus it is inferred, that the lead halide complexes show a slight decrease in stability as the size of the halide ion decreases. Similar conclusions have been reached by Arhland, in his study of the stability of metal halide complexes in aqueous solutions(1). The increase in $a_{PbCl_2}$ with increasing temperature, for compositions between 30 and 70 mole % $PbCl_2$, may therefore be explained by the tendency for dissociation of the complex ions (i.e. the formation of "free" $Pb^{2+}$ and $Cl^-$ ions) with increased thermal vibration, to predominate over the increased tendency to form ion pairs.

The inverted temperature dependence of the activity of $PbCl_2$, for mixtures containing 75-85 mole % $PbCl_2$ in the system $PbCl_2$-CsCl, may not be real as it falls within experimental error.

b) Free energies

The dependence of the partial molar free energies of lead chloride and cesium chloride on composition, are shown in fig. 3.24. Apart from a greater negative value and the slight maximum in $\Delta\bar{G}_1$ at about 85 mole % $PbCl_2$, they are very similar to the partial molar free energies of the components in the system $PbBr_2$-CsBr, at corresponding compositions. The magnitude of the positive value for the excess chemical potential of $PbCl_2$, is very much smaller than that

---

1. Arhland: Acta Chem. Scand., 10 723 (1956)

for $PbBr_2$ in the corresponding bromide system and is indicative of a much lower energy to dissociate $PbCl_2$ molecules. The proportion of undissociated lead chloride molecules in the standard state is therefore considered lower than in pure lead bromide. (This ties up with the explanation of smaller positive deviations of $a_{PbCl_2}$ than $a_{PbBr_2}$ in the $PbX_2$-CsX systems.)

Integral free energies of $PbCl_2$-CsCl solutions are plotted in fig. 3.24 and the excess quantities, calculated using eqns. 4.12-4.14, are given in Table 4.18a. The estimated composition for the maximum

TABLE 4.18a

Excess integral free energies in the system $PbCl_2$-CsCl at 700°C

| mole fraction $PbCl_2$ ($N_1$) | mole fraction CsCl ($N_2$) | $-\Delta G$(ideal) (K cal/mole) | $-\Delta G^E$ (K cal/mole) |
|---|---|---|---|
| 0.10 | 0.90 | 0.630 | 2.87 |
| 0.20 | 0.80 | 0.968 | 3.96 |
| 0.30 | 0.70 | 1.182 | 4.19 |
| 0.40 | 0.60 | 1.302 | 4.12 |
| 0.50 | 0.50 | 1.340 | 3.82 |
| 0.60 | 0.40 | 1.302 | 3.31 |
| 0.70 | 0.30 | 1.182 | 2.64 |
| 0.80 | 0.20 | 0.968 | 1.87 |
| 0.90 | 0.10 | 0.630 | 0.96 |

Estimated position of maximum deviation = 0.32 m.f. $PbCl_2$

Estimated value for $\Delta G^E$ (max.) = -4.20 K cal/mole

value of $\Delta G^E$, corresponds very closely to that for the system $PbBr_2$-CsBr, but the value of the excess quantity is more negative by approximately 1.0 K cal/mole. If, however, the partial molar free energies of $PbCl_2$ and $PbBr_2$ are compared at similar temperatures (see Tables 3.19 and 3.27), then although the values still differ in the same sense, the magnitude of the deviation is much smaller and hence the difference between $\Delta G^E$ derived from $\Delta\bar{G}_{PbX_2}$ for the two systems will be less (estimated at approximately 250 cals/mole).

c) Enthalpies and Entropies

Even allowing for an error of ± 500 cals/mole in the enthalpy values, $\Delta\bar{H}_{PbCl_2}$ shows an increasing negative value as the proportion of CsCl is increased from 30 mole % (see fig. 3.25). This is consistent with an increased tendency to form complex ions as the proportion of CsCl in the melt increases (see the relevant discussion for the systems $PbBr_2$-MBr). The initial negative change of enthalpy in mixtures containing 90-100 mole % $PbCl_2$, does not have any significance, as the magnitude of the minimum is of the same order as the error in the calculation.

The partial molar entropy of $PbCl_2$ shows, apart from two minima, increased positive values as the proportion of alkali chloride increases (see fig. 3.25). Owing to the magnitude of the error in this thermodynamic quantity (± 0.8 cal/deg/mole) and in the excess quantity, it is very doubtful whether such minima can be regarded as physically significant. The excess positive entropy for lead chloride, is accounted for by the contribution to the entropy of an

excess volume change on mixing, as in the systems $PbBr_2$-MBr. This effect is regarded as being greater than the ordering due to complex ion formation. In comparing this system with that of the corresponding bromide system, it is apparent that the partial molar entropy of $PbCl_2$ approaches more closely the ideal values. This may be due to increased stability of the complex species, to a decrease in the excess free volume of the mixtures, or to heat of mixing effects, all of which could result in a lowering of the partial entropy of that component. It can be predicted from electro-negativity data, that the "bond" between lead and chlorine, should possess less co-valent character than that between lead and bromine, in complex ions $PbCl_n^{(n-2)-}$ and $PbBr_n^{(n-2)-}$ respectively. It follows that Pb—Cl complex ions should tend to be less stable than Pb — Br complex ions (see Sect.4B.1b). Because the halide ion is the larger in the $PbBr_2$-CsBr system, the excess free volume may be larger for this system than for the $PbCl_2$-CsCl system, hence, the contribution of the free volume to the partial molar entropy of $PbBr_2$ would be greater.

## 4B.2 THE THREE COMPONENT SYSTEMS (x $PbCl_2$ + x CsCl) —— (1 - 2x)MCl (WHERE M = Li, Na, K, Rb)

### a) Activity of the components

The following activity results will be discussed, assuming that the stability of complex ions is influenced by the proportion of more polarizing $M^+$ species relative to that of the less polarizing $Cs^+$ ion. The effect of increased temperature, as in the previous systems, will be regarded as resulting from the relative dominance of two effects: (a) the tendency for dissociation of complex ions to take place due to thermal vibration, and (b) the tendency for increased "ion pair" formation with rising temperature.

Table 4.19 represents the deviations from the Temkin activity as a function of the mole fraction of the components and of the mole fraction ratio CsCl:MCl. In order to find some correlation between the activity of the components and the ratio of CsCl:MCl, the quantity $\Delta a_{PbCl_2}$ is plotted against log ((mole fraction CsCl)/(mole fraction MCl)). Here $\Delta a_{PbCl_2}$ is the percentage deviation of the experimental activity from the Temkin value. These curves are illustrated in fig. 4.12. It has been assumed, in calculating both the mole fraction of MCl and CsCl, that the concentration of CsCl is equal to the concentration of $PbCl_2$. (With reference to the tables in Chapter 3, $N_{CsCl} = N_{PbCl_2} \pm 2\text{-}5\%$.)

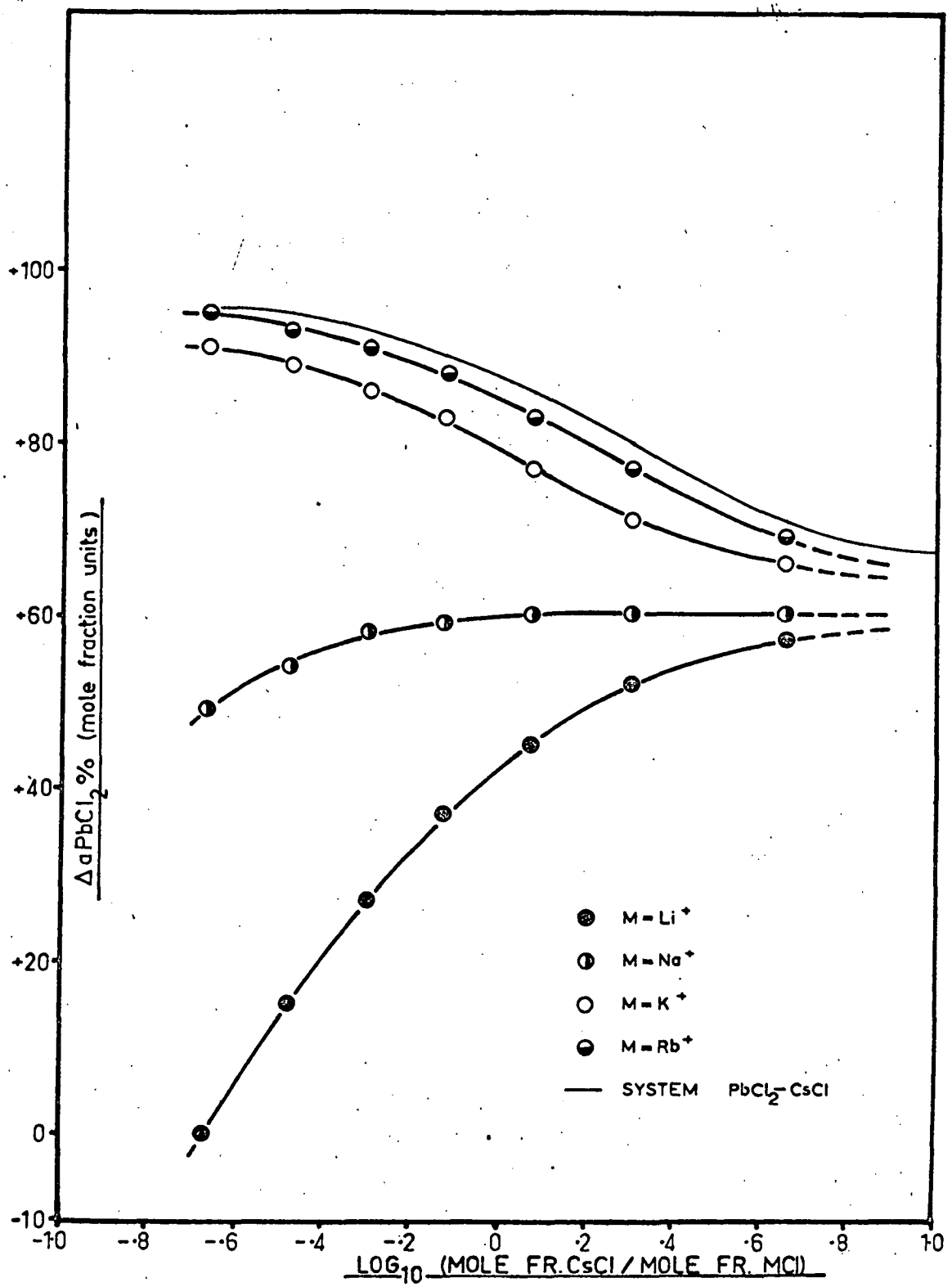



FIG. 4·12

SYSTEM $(x\,PbCl_2 + x\,CsCl) - (1-2x)\,MCl$ (700°C)
% DEVIATION $aPbCl_2$ FROM TEMKIN ACTIVITY AS A FUNCTN. OF THE RATIO m.f. CsCl / m.f. MCl

TABLE 4.19

Series ($x\ PbCl_2 + x\ CsCl$) —— $(1 - 2x)MCl$ (700°C)
Deviations in the activity of $PbCl_2$ from the ideal Temkin activity

| m.f. $PbCl_2$ | m.f. CsCl | m.f. MCl | $\frac{CsCl}{MCl}$ | $\log.\frac{CsCl}{MCl}$ | $-\Delta a_{PbCl_2}$ (%), (M = | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $Cs^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ |
| 0.15 | 0.15 | 0.70 | 0.214 | -0.670 | 95 | 0 | 49 | 91 | 95 |
| 0.20 | 0.20 | 0.60 | 0.33 | -0.477 | 95 | 15 | 54 | 89 | 93 |
| 0.25 | 0.25 | 0.50 | 0.50 | -0.301 | 92 | 27 | 58 | 86 | 91 |
| 0.30 | 0.30 | 0.40 | 0.75 | -0.125 | 90 | 37 | 59 | 83 | 88 |
| 0.35 | 0.35 | 0.30 | 1.17 | +0.068 | 86 | 45 | 60 | 77 | 83 |
| 0.40 | 0.40 | 0.20 | 2.00 | +0.301 | 80 | 52 | 60 | 71 | 77 |
| 0.45 | 0.45 | 0.10 | 4.50 | +0.653 | 71 | 57 | 60 | 66 | 69 |
| 0.50 | 0.50 | 0.00 | $\infty$ | $+\infty$ | 61 | - | - | - | - |

(i) The system ($x\ PbCl_2 + x\ CsCl$) —— $(1 - 2x)LiCl$

As the concentration of LiCl is increased to 70 mole % LiCl, the activity and activity coefficient of $PbCl_2$ show a tendency to approach more ideal values. For mixtures containing more than 70 mole % LiCl, $a_{PbCl_2}$ exhibits positive deviations from the ideal values, which are presumed to decrease to zero as the mole fraction of $PbCl_2$ tends to zero. This is consistent with the view that as the ratio of CsCl to MCl decreases, so does the stability of complex ions of the form $PbCl_n^{(n-2)-}$ decrease. When $CsCl/MCl < 0.214$, then the only prevalent tendency is the dissociation of species present in pure lead chloride which yield an increase in the number of "free" $Pb^{2+}$ and $Cl^-$ ions and produce an activity in excess of that predicted by the Temkin model.

For the system $PbCl_2$-LiCl, Lantratov and Alabyshev[1] found positive deviations of the activity from the Temkin values over the whole composition range and Markov et al.[2] observed positive deviations for various compositions.

In the system $PbCl_2$-CsCl, the effect of increasing the temperature was observed to cause a slight increase in the activity of lead chloride. The reverse was true for the system $PbBr_2$-CsBr. This was attributed to the lead-chlorine "bonds" being more susceptible to polarization than the lead-bromine bonds in the complex $PbX_n^{(n-2)-}$. The main effect in the chloride system was therefore an increase in dissociation with increase in temperature. In the binary lead bromide-cesium bromide system, on the other hand, the dissociation of complex ions with increased temperature was inhibited to a certain extent (due to the increased strength of the Pb — Br "bond"), so that the resultant effect was increased ion association within the melt, and hence reduced activity of $PbBr_2$. With RbBr and to a greater extent with KBr, the polarization of the "bonds" of the complexes was sufficient to allow the dissociation process to become relatively more important than the tendency for "ion pair" formation to take place. In respect of systems of the types $PbX_2$-NaX and $PbX_2$-LiX, complex ions are assumed to be so unstable that such mixtures are likely to exist largely as discrete, simple ions. For solutions containing $Pb^{2+}$, $Li^+$ and $Cl^-$, in fact, evidence suggests that there are no complex ions (see earlier in this Section). For binary systems of which one component is either

---

1. Lantratov and Alabyshev: Zhur. Priklad. Khim., 26 263 (1953)
2. Markov, Delimarskii and Panchenko: Zhur. Fiz. Khim., 29 51 (1955)

$Li^+$ or $Na^+$, temperature increase will promote negligible dissociation but will stimulate an increase in ion pair formation in the melt. Thus, one would expect such systems to exhibit a decrease in activity with increasing temperature. This is observed in the binary systems $PbBr_2$-NaBr and $PbCl_2$-LiCl, investigated by Lantratov and Shevlyakova[1] and Lantratov and Alabyshev[2], respectively.

In the present system, for compositions between 0.33 and 0.50 mole fraction $PbCl_2$, i.e. until the ratio CsCl to LiCl diminishes to 1.0, the concentration of complex species in the melt is sufficiently high, for an increase in temperature to cause a greater overall dissociation. This explains the increase in $a_{PbCl_2}$, although the magnitude of the deviations are much larger than anticipated. As the ratio of $Li^+$:$Cs^+$ increases, the concentration of the species $PbCl_n^{(n-2)-}$ would be expected to decrease due to the increasing polarization of the Pb — Cl "bonds" of the complex ions. The most predominant effect of an increase in temperature, for solutions where $Li^+/Cs^+ > 1$, would therefore tend to be a decrease in the number of "free" $Pb^{2+}$ and $Cl^-$ due to ion pair formation, rather than the reverse effect due to thermal dissociation; a decrease in $a_{PbCl_2}$ could then be predicted. This is observed experimentally in the system $(x\ PbCl_2 + x\ CsCl)$ —— $(1 - 2x)$ LiCl, for mixtures containing 0-33 mole % $PbCl_2$.

---

1. Lantratov and Shevlyakova: Russ. J. Inorg. Chem., 6 95 (1961)
2. Lantratov and Alabyshev: Zhur. Priklad. Khim., 26 263 (1953)

(ii) The system (x $PbCl_2$ + x CsCl) —— (1 - 2x)NaCl

Pb — Cl complex species tend to be unstable in the presence of NaCl, although this effect is less marked for NaCl than for LiCl. For mixtures whose composition falls in the range $N_{NaCl} \ll N_{CsCl}$ to $N_{NaCl} = N_{CsCl}$ (where Na refers to the mole fraction of component "a"), the deviations in activity are constant, indicating that in this region of composition, sufficient $Cs^+$ ions are present to "screen" the complex ions, to a certain extent, from the polarizing influence of $Na^+$ ions. In the case of the lithium ion, which is 2.5 times more polarizing than the sodium ion, the electrostatic forces are able to overcome this "screening" effect, so that polarization of the Pb — Cl "bonds" of the complex species is not inhibited by the $Cs^+$ ions present. For mixtures for which the ratio CsCl/NaCl < 1.0, both the activity deviations from the Temkin value and the activity coefficient of $PbCl_2$, show a tendency to become more nearly ideal. As the concentration of CsCl and $PbCl_2$ tend to zero, so does the polarization of the "bonds" of the complex ions increase and thereby leads to an increased proportion of "free" $Pb^{2+}$ and $Cl^-$ ions in the solution.

The effect of increasing temperature can be explained in exactly the same way as for the system (x $PbCl_2$ + x CsCl) —— (1 - 2x) LiCl. From 0.5 to 0.3 mole fraction $PbCl_2$ (approximately the range CsCl/NaCl = 1-$\infty$), the proportion of complex ions is still sufficiently high to produce an increased number of simple ions, due to the dissociation of complex species at higher temperatures. The more pronounced reduction in the number of complex ions for compositions

between 0 and 30 mole % $PbCl_2$, allows for ion association to become more important than for mixtures containing 30 to 50 mole % $PbCl_2$, as the temperature is raised.. The decreased polarizing power of the $Na^+$ ion compared to the $Li^+$ ion, gives rise to a somewhat lesser dissociation of complex species and hence the smaller decrease in the activity of $PbCl_2$ for a similar temperature rise, in the present system compared with the system (x $PbCl_2$ + x CsCl) —— (1 - 2x)LiCl.

(iii) The systems (x $PbCl_2$ + x CsCl) —— (1 - 2x)KCl,
(x $PbCl_2$ + x CsCl) —— (1 - 2x)RbCl

From the graphs of the activity and activity coefficient of lead chloride as functions of composition, it can be seen that, for both these systems, the $K^+$ and $Rb^+$ ions produce far less dissociation of the complex ions than either $Li^+$ or $Na^+$. For both of the former systems, the deviations from the Temkin activity of $a_{PbCl_2}$ show a continual increase as the ratio of CsCl to MCl decreases. Although this effect is less marked than for the system $PbCl_2$-CsCl, this would be expected, as the polarizing powers of $Rb^+$ and $K^+$ (in this order) are progressively greater than that of the $Cs^+$ ion. Thus the stability of the complexes $PbCl_n^{(n-2)-}$, show anslightly greater decrease, (and the activity of $PbCl_2$ shows an increase) from the system (x $PbCl_2$ + x CsCl) —— (1 - 2x)RbCl to the system (x $PbCl_2$ + x CsCl) —— (1 - 2x)KCl.

Since the complex ions in both these systems are largely unaffected by the presence of $K^+$ and $Rb^+$ (e.g. the deviations of $a_{PbCl_2}$ from the Temkin activity are similar to those for $a_{PbCl_2}$ in the system $PbCl_2$-CsCl), increase in temperature should have the same effect

on the activity as for the system $PbCl_2$-CsCl. Thus an increase in the numbers of "free" ions should result, due to increase in thermal vibration of the complex ions. This is observed experimentally in both systems. The very slight displacement in the opposite direction at the 40 mole % $PbCl_2$ composition in the system (x $PbCl_2$ + x CsCl) —— (1 - 2x)KCl, is attributed to experimental error.

As the proportion of CsCl (relative to MCl) decreases, the tendency to dissociate complex ions is increased by the presence of $Li^+$ and $Na^+$ , but is only slightly affected by $Rb^+$ and $K^+$ . In the case of lithium and sodium, when the concentration of MCl > CsCl, the proportion of complex ions decreases to such an extent, that an increase in temperature produces a decrease in the activity of $PbCl_2$ due to increased ion pair formation. When MCl < CsCl, for the systems containing $Li^+$ and $Na^+$ and for all values of CsCl/MCl with $K^+$ and $Rb^+$, the higher concentration of complexes is sufficient to produce an increase in the activity of $PbCl_2$ with increase of temperature, due to the dissociation of complex ions.

b) Free energies

The partial molar free energies and excess free energy functions of $PbCl_2$ are plotted in figs. 3.39-3.42. The tendency shown by $\Delta\bar{G}_1$ and $\Delta\bar{G}_1^E$, to deviate from the corresponding quantities for the system $PbCl_2$-CsCl, is indicative of increased dissociation of complex ions, as the cesium ion is replaced by alkali metal ions of higher polarizing power. Because these thermodynamic quantities are

related to the activity of lead chloride, the chemical potentials of $PbCl_2$ for each system will not be discussed separately.

In fig. 3.43, are plotted $\Delta(\Delta\bar{G}_l)$, i.e., the deviations of the partial molar free energies of lead chloride in the systems (x $PbCl_2$ + x CsCl) —— (1 - 2x)MCl, from those in the binary system $PbCl_2$-CsCl, as functions of the ratio MCl/CsCl. Taking into account the errors in $\Delta(\Delta\bar{G}_l)$ and in the calculation of the alkali halide ratio (see Sections 3.2c and 4B.2a), a linear dependence of $\Delta(\Delta\bar{G}_l)$ on alkali halide ratio is noted. Whether the change in slope of the plots for $Li^+$ and $Na^+$, has any significance or not, is doubtful. It could, however, be due to some difference in the interaction of the polarizing fields of the alkali metal ions with the Pb — Cl "bonds" of the complex ions. Generally, however, the deviation in the chemical potential of lead chloride increases in direct proportion to the ratio of MCl to CsCl.

c) Entropies

Table 4.20 and fig. 4.13, contain a summary of the excess partial molar entropies of lead chloride for each of the systems (x $PbCl_2$ + x CsCl) —— (1 - 2x)MCl. The values for each composition are estimated from the tables in Section 3. The value of $\Delta\bar{S}_{PbCl_2}$, for the system $PbCl_2$-CsCl, is also included for comparison. Inaccuracies in the calculated values in tables 3.41-3.44, as well as those introduced by estimation in Table 4.20, preclude an accurate comparison of the excess partial entropies. Hence, only the trend in the properties with respect to (a), increasing proportions of MCl, and

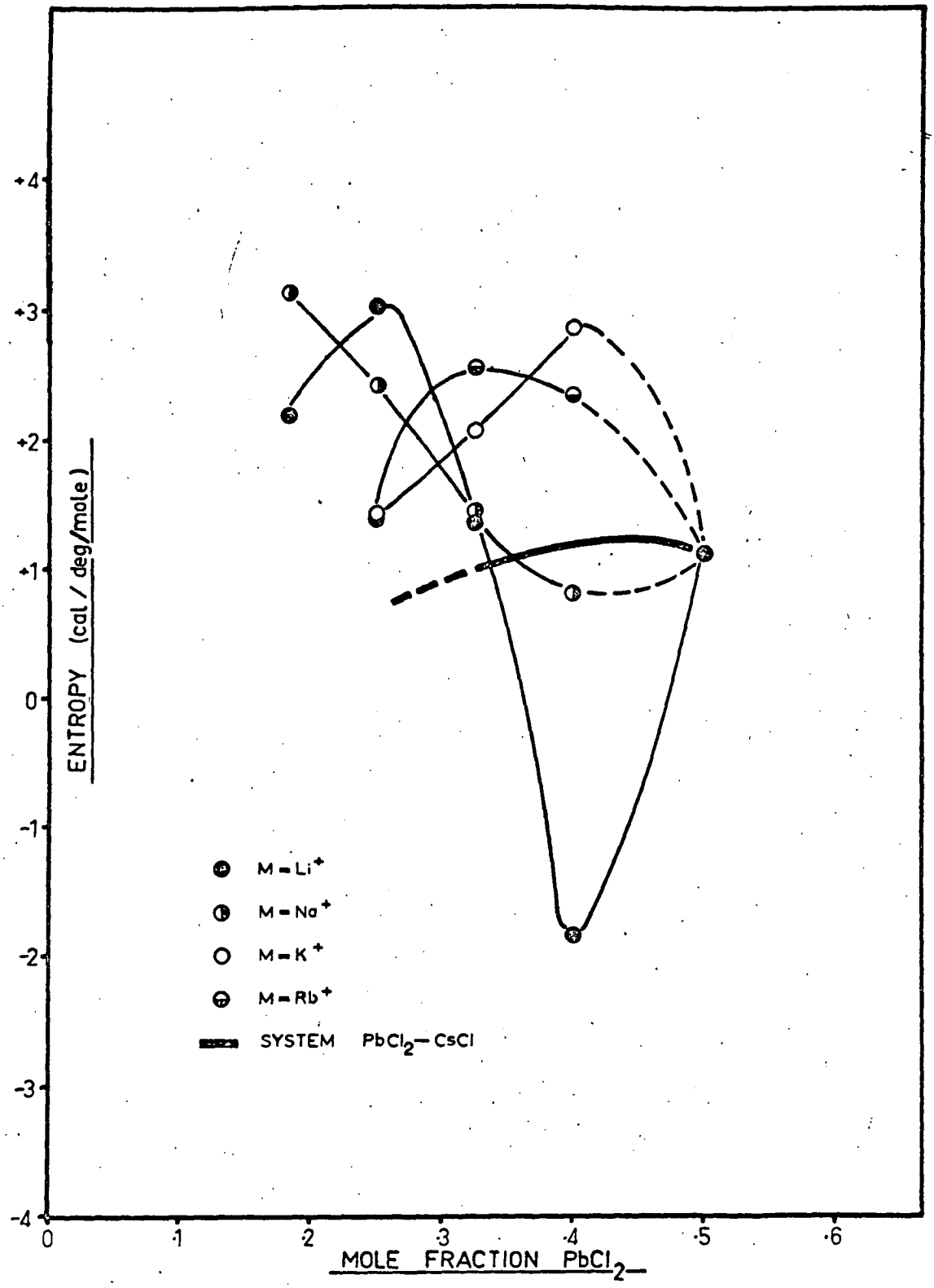



FIG. 4·13 EXCESS PARTIAL ENTROPY OF $PbCl_2$ IN THE SYSTEMS $(x\,PbCl_2 + x\,CsCl) — (1-2x)\,MCl$ (700°C)

TABLE 4.20

Comparison of the excess partial molar entropies in the systems

$(x\ PbCl_2 + x\ CsCl)$—— $(1 - 2x)MCl$ (700°C)

| m.f. $PbCl_2$ | m.f. CsCl | m.f. MCl | CsCl / MCl | $\Delta\bar{S}_1^E$ (cals/deg/mole), M = | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Cs^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ |
| 0.500 | 0.500 | - | ∞ | +1.10 | - | - | - | - |
| 0.400 | 0.400 | 0.200 | 2.00 | +1.20 | -1.85 | +0.80 | +2.88 | +2.34 |
| 0.325 | 0.325 | 0.350 | 0.93 | +1.00 | +1.35 | +1.44 | +2.07 | +2.55 |
| 0.250 | 0.250 | 0.500 | 0.50 | - | +3.02 | +2.41 | +1.42 | +1.38 |
| 0.150 | 0.150 | 0.700 | 0.21 | - | +2.18 | +3.13 | - | - |

(b) increasing ionic radius of $M^+$, will be discussed.

For most mixtures over the composition range studied, the excess partial molar entropy of $PbCl_2$ is greater than those values appropriate to the corresponding mole fractions of $PbCl_2$ in the system $PbCl_2$-CsCl. Unfortunately, no mixtures containing less than 30.7 mole % $PbCl_2$ were investigated for the latter system, so that for mixtures more dilute in $PbCl_2$, no comparison can be made. Generally the introduction of smaller, more polarizing ions relative to $Cs^+$, will have two effects on the entropy of mixing (see Section 4A.5) : (a) decrease in the molar volume of the mixture, which contributes to a decrease in the entropy and (b) decrease in the concentration of complex ions, which results in an increase in entropy. From the values of $\Delta\bar{S}^E_{PbCl_2}$ with additions of MCl to solutions of $PbCl_2$ and CsCl (where M = Li, Na, K, Rb) the dissociation of the complex ions appears to be the more dominant effect.

Initially it appears that additions of LiCl to a mixture of lead chloride and cesium chloride, cause a sharp increase of order within the melt*. This is attributed to a rapid decrease in the molar volume of the solution. The sharp increase in the excess partial molar entropy for values of the mole ratio CsCl:LiCl < 2.0, can be explained by the rapid dissociation of complex ions by the highly polarizing $Li^+$ ion.

d) Enthalpies

In Table 4.21, are summarized the partial molar enthalpies of $PbCl_2$ for the three component systems, and for the system $PbCl_2$-CsCl. Because similar approximations have been made to obtain the data in Tables 4.20 and 4.21, the error in the following values for $\triangle \bar{H}_1$, are relatively large (approximately 500 cals/mole). The

TABLE 4.21

Comparison of the partial molar enthalpies of $PbCl_2$ in the systems $(x\ PbCl_2 + x\ CsCl) \rightarrow (1 - 2x)MCl$ (700°C)

| m.f. $PbCl_2$ | m.f. CsCl | m.f. MCl | CsCl / MCl | $-\triangle\bar{H}_1$ (K cal/mole), M = $Cs^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ |
|---|---|---|---|---|---|---|---|---|
| 0.500 | 0.500 | - | ∞ | +0.67 | - | - | - | - |
| 0.400 | 0.400 | 0.200 | 2.00 | +2.10 | +2.84 | +1.03 | -0.43 | +0.58 |
| 0.325 | 0.325 | 0.350 | 0.93 | +3.00 | -0.22 | +0.31 | +1.25 | +1.37 |
| 0.250 | 0.250 | 0.500 | 0.50 | - | -2.14 | -0.59 | +2.38 | +3.32 |
| 0.150 | 0.150 | 0.700 | 0.21 | - | -1.96 | -1.73 | - | - |

* A similar tendency is noted for low concentrations of NaCl. However, in this case, the deviation of $\triangle \bar{S}_1^E$ from the value for the system $PbCl_2$-CsCl is less than the experimental error.

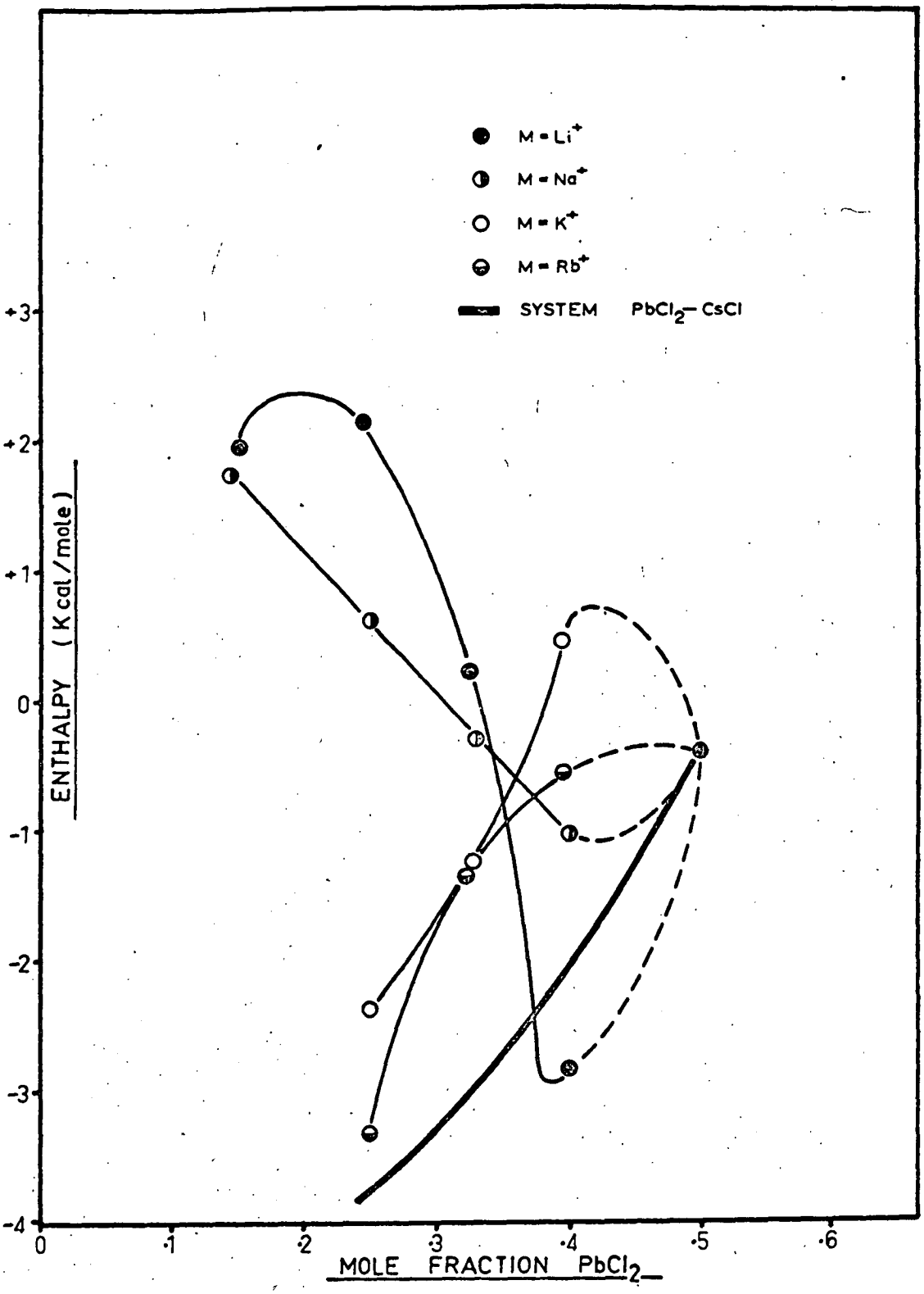



FIG. 4·14

PARTIAL MOLAR ENTHALPIES OF $PbCl_2$ IN THE SYSTEMS $(xPbCl_2 + xCsCl) — (1-2x)MCl$ (700°C)

thermodynamic quantities are plotted in fig.4.14.

Apart from the large negative value for $\Delta\bar{H}_{PbCl_2}$ in the system (x $PbCl_2$ + x CsCl) —— (1 - 2x)LiCl, the partial molar enthalpies for lead chloride in the three component mixtures all show more positive values than those for the corresponding binary system $PbCl_2$-CsCl. From the investigations of McCarty and Kleppa[1] on the systems $PbCl_2$-MCl (where M = Li, Na, K, Rb, Cs), the magnitude of the negative deviations of the partial enthalpy of lead chloride from the ideal solution values, are assumed to bear a direct relationship to the degree of complex ion formation within these systems. Thus, as the ratio of CsCl to MCl decreases below 2.0 in the systems involving lithium and sodium ions, $\Delta\bar{H}_{PbCl_2}$ shows increasing positive values which are attributed to the breakdown of complex ions. For the systems containing $K^+$ and $Rb^+$, increasing negative values of $\Delta\bar{H}_{PbCl_2}$ (as the mole fraction of $PbCl_2$ decreases) are assumed to be due to an increase in complex ion formation. The only effect of replacing $Cs^+$ with $K^+$ or $Rb^+$, is to reduce the stability of the associated species of lead and chlorine to a slight extent. However, neither are sufficiently polarizing (compared to $Li^+$ or $Na^+$) to induce extensive dissociation.

---

1. McCarty and Kleppa: J. Phys. Chem., 68 3846 (1964)

## 4B.3 THE THREE COMPONENT SYSTEMS $(2x\ PbCl_2 + x\ CsCl) \rightleftharpoons (1 - 3x)MCl$ (WHERE M = Li, Na, K, Rb)

### a) Activity of the components

The deviations of $a_{PbCl_2}$ from the Temkin activity, as functions of the mole fraction of the components and of the ratio CsCl/MCl, are presented in Table 4.22. The quantity $\Delta a_{PbCl_2}$ (%) versus log. ((mole fraction CsCl)/(mole fraction MCl)) is plotted in fig. 4.15. The same assumptions apply to the calculations of the mole fraction ratio as to the systems $(x\ PbCl_2 + x\ CsCl) \rightleftharpoons (1 - 2x)MCl$.

TABLE 4.22

Systems $(2x\ PbCl_2 + x\ CsCl) \rightleftharpoons (1 - 3x)MCl$ (700°C)
Deviations of $a_{PbCl_2}$ from the Temkin activity

| m.f. $PbCl_2$ | m.f. CsCl | m.f. MCl | $\frac{CsCl}{MCl}$ | $\log.\frac{CsCl}{MCl}$ | $-\Delta a_{PbCl_2}$ (%), $M^+$ = | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $Cs^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ |
| 0.20 | 0.100 | 0.700 | 0.14 | -0.854 | 95 | -1.2 | 33 | 83 | 92 |
| 0.25 | 0.125 | 0.625 | 0.20 | -0.699 | 92 | -11 | 28 | 82 | 90 |
| 0.30 | 0.150 | 0.550 | 0.27 | -0.569 | 90 | - 9 | 23 | 79 | 87 |
| 0.35 | 0.175 | 0.475 | 0.37 | -0.432 | 86 | - 2 | 22 | 74 | 82 |
| 0.40 | 0.200 | 0.400 | 0.50 | -0.301 | 80 | 15 | 27 | 67 | 76 |
| 0.45 | 0.225 | 0.325 | 0.69 | -0.161 | 71 | 19 | 33 | 59 | 68 |
| 0.50 | 0.250 | 0.250 | 1.00 | 0.000 | 61 | 22 | 27 | 51 | 59 |
| 0.55 | 0.275 | 0.175 | 1.57 | +0.200 | 51 | 23 | 23 | 44 | 47 |
| 0.60 | 0.300 | 0.100 | 3.00 | +0.480 | 40 | 24 | 23 | 35 | 36 |

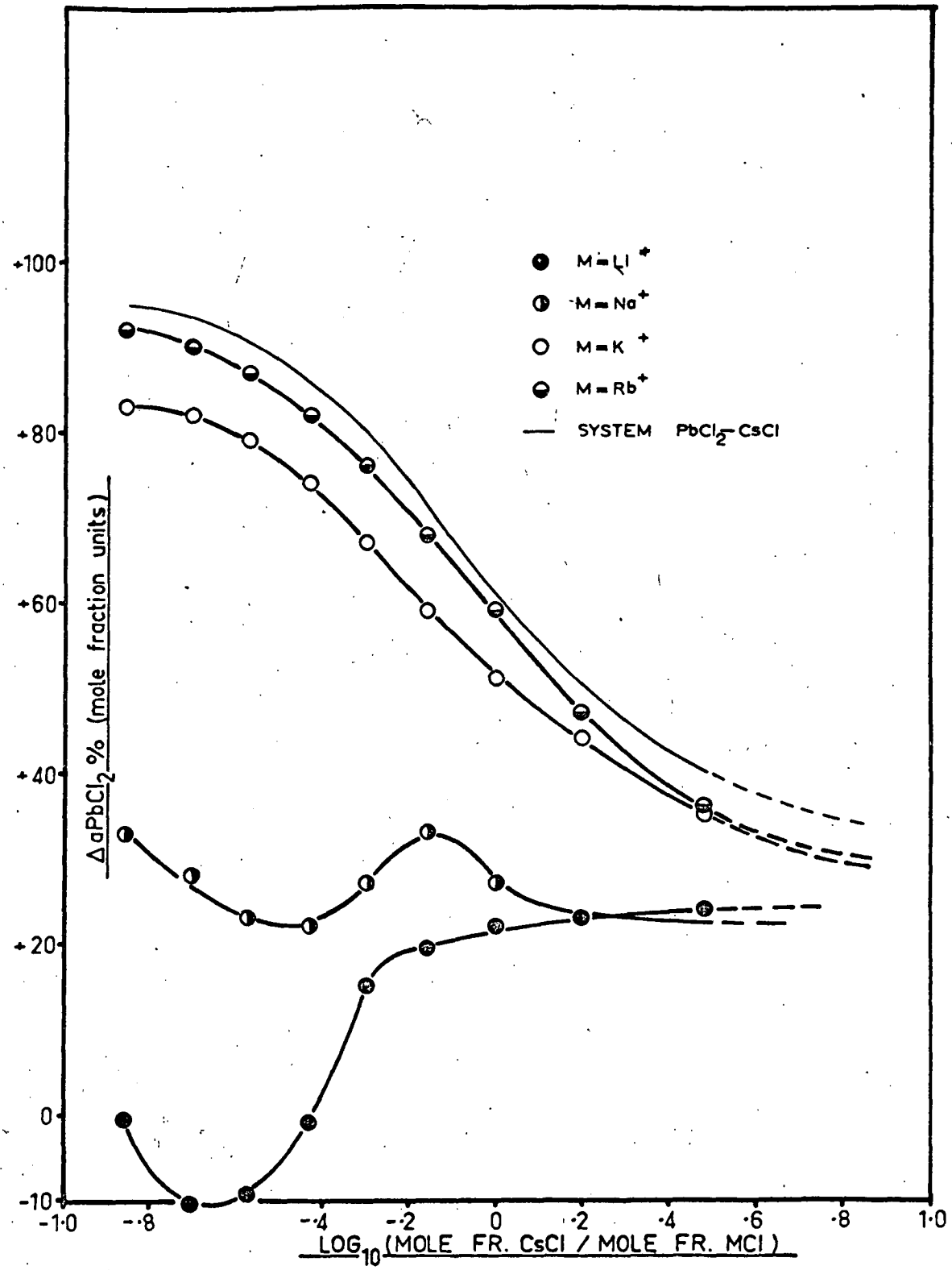



FIG. 4·15

SYSTEM $(2x\,PbCl_2 + x\,CsCl) - (1-3x)\,MCl$ (700° C)
% DEVIATION $aPbCl_2$ FROM TEMKIN ACTIVITY AS A FUNCTION OF THE RATIO mf. CsCl / mf. MCl

(i) The system $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)LiCl$

As the mole fraction of LiCl is increased to 40 mole % ($CsCl/MCl \approx 0.5$, mole fraction LiCl = mole fraction $PbCl_2$), the activity coefficient of $PbCl_2$ gradually approaches its ideal value. When the concentration of cesium chloride exceeds that of lead chloride, this tendency becomes more pronounced. Initially, additions of LiCl are presumed to cause a decrease in the concentration of complex species, due to the dissociation of the Pb — Cl complex ions resulting from polarization of the Pb — Cl "bonds". Later, when $Li^+$ ions are in excess of the $Pb^{2+}$ ions, the tendency is for all complex ions and undissociated lead chloride molecules (present in the standard state of pure $PbCl_2$) to be dissociated into single ions of $Pb^{2+}$ and $Cl^-$, an effect which finally results in positive deviations of $a_{PbCl_2}$ above the Temkin activity.

For all mixtures of the system $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)LiCl$ investigated, the activity of lead chloride decreases with increasing temperature. This can be explained, if the concentration of complex ions is at no stage sufficiently high for the thermal dissociation of these ions to be of any importance, compared with the general increase in ion association (as ion pairs) in the melt. In the system $PbCl_2$-CsCl (i.e. the limit of the system $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)LiCl$ when the mole fraction of LiCl is zero), the concentration of complex ions at 66 mole % $PbCl_2$, is much less than at 50 mole % $PbCl_2$. This deduction follows from the analogy with deviations of the activity of $PbCl_2$ from the ideal value in the system,

i.e., 29% at 0.66 mole fraction $PbCl_2$ and 61% at 0.50 mole fraction $PbCl_2$. Hence, the effect of increase of temperature on the overall dissociation of the complexes, will be considerably less in the three component system $(2x\ PbCl_2 + x\ CsCl) \longrightarrow (1 - 3x)LiCl$, than in the system $(x\ PbCl_2 + x\ CsCl) \longrightarrow (1 - 2x)LiCl$ - hence the tendency for ion association in the melt to increase, will be more marked.

(ii) <u>The system $(2x\ PbCl_2 + x\ CsCl) \longrightarrow (1 - 3x)NaCl$</u>

In the composition range studied, the activity of lead chloride is closer to its ideal value for this system than for the binary system $PbCl_2$-CsCl. As in the previous series where lead chloride and cesium chloride are in the ratio 1:1 however, the $Na^+$ ion has a less pronounced effect than that of the $Li^+$ ion. Taking into account the likely errors in the activity at 0.561 mole fraction $PbCl_2$ (approximately $\pm$ 0.1 units), $a_{PbCl_2}$ shows a linear dependence on the function log. ((mole fraction CsCl)/(mole fraction NaCl)), similarly to the behaviour in the system $(x\ PbCl_2 + x\ CsCl) \longrightarrow (1 - 2x)NaCl$, for the initial additions of NaCl. The activity of lead chloride can therefore be interpreted in the same way, with reference to the "screening" action of the $Cs^+$ ion. For mixtures whose compositions are close to equimolar, in NaCl and $PbCl_2$, this effect is largely nullified and the concentration of complex species shows a more rapid decrease as the mole fraction of NaCl increases, until the stage at which the interactions within the melt are assumed to be of the same type and magnitude as in the system $PbCl_2$-NaCl. Thus, when the mole ratio CsCl/MCl is less than about 0.35, the activity of lead chloride approximates to that in the system $PbCl_2$-NaCl (investigated by

Lantratov and Alabyshev[1].)

Over most of the composition range studied, increase in temperature stimulates an increase in ion pair formation in the melt. Because the concentration of complex species is presumed to be somewhat greater in this system than in the corresponding lithium chloride system, the contribution to the activity of "free" ions, resulting from the thermal dissociation of such species, will be larger and the negative deviations of the activity from the 700°C isotherm will be less. This is observed experimentally. The value for $a_{PbCl_2}$ at 800°C for the mixture containing 56.1 mole % $PbCl_2$, deviates in the opposite sense from the value at 700°C and apart from experimental error, no other explanation can be offered.

(iii) The systems $(2x\ PbCl_2 + x\ CsCl) \text{ —— } (1 - 3x)KCl$, $(2x\ PbCl_2 + x\ CsCl) \text{ —— } (1 - 3x)RbCl$

The activity and activity coefficients for $PbCl_2$ in both these systems, show increasing deviations from those values expected of an ideal solution. The deviations increase slightly as the size of the alkali metal ion is increased and a similar interpretation as that proposed for the systems $(x\ PbCl_2 + x\ CsCl) \text{ —— } (1 - 2x)KCl$ and $(x\ PbCl_2 + x\ CsCl) \text{ —— } (1 - 2x)RbCl$ can be applied. It can thus be concluded, that whereas the stabilities of complex ions are very dependent on the ionic radii (r), of alkali metal ions for values of r less than 1Å (e.g. $Li^+$, $Na^+$), they are comparatively insensitive to the actual size of $M^+$ when r is greater than 1Å (e.g. $K^+$, $Rb^+$ and $Cs^+$).

---

1. Lantratov and Alabyshev: Zhur. Priklad. Khim., 26 263 (1953)

Because of the inferred increased concentration of complex ions in these systems, compared with the systems (2x $PbCl_2$ + x CsCl) —— (1 - 3x)LiCl and (2x $PbCl_2$ + x CsCl) —— (1 - 3x)NaCl, an increase of temperature will cause increased dissociation of such species. This explanation is completely analagous to that given for the systems (x $PbCl_2$ + x CsCl) —— (1 - 2x)RbCl and (x $PbCl_2$ + x CsCl) —— (1 - 2x)KCl. Thus there is an overall increase in the activity of $PbCl_2$ with increase of temperature, up to approximately 45 mole % lead chloride. For solutions richer in $PbCl_2$, up to the limit when CsCl/MCl = 0, increased temperature has the reverse effect. A similar tendency is noted for mixtures containing more than 70 mole % $PbCl_2$ in the system $PbCl_2$-CsCl. No satisfactory explanation can be offered for the temperature coefficient of $a_{PbCl_2}$ in this composition region.

The relative effect of the polarizing power ( = $f(1/r^2)$) of the alkali metal ions on the complex Pb — Cl species in this series, is essentially the same as the previous series having the higher ratio of $PbCl_2$ to CsCl. The main difference in the values of $a_{PbCl_2}$ in the two series (x $PbCl_2$ + x CsCl) —— (1 - 2x)MCl and (2x $PbCl_2$ + x CsCl) —— (1 - 3x)MCl, is in the magnitude of the deviations from the Temkin activity at similar mole ratios of CsCl to MCl. This, by analogy with the system $PbCl_2$-CsCl, is assumed to be due to a higher concentration of complex ions in the former case.

b) Free energies

The partial molar free energies and excess free energy functions of lead chloride, are plotted in figs. 3.39-3.42. The variations of the partial molar free energy and the excess free energy of $PbCl_2$ (with respect to the system $PbCl_2$-CsCl), are interpreted, as before, as indicating decreased concentration of complex ions as the radius of $M^+$ is decreased in the systems (2x $PbCl_2$ + x CsCl) —— (1 - 3x)MCl. The results for the systems fall into two categories, depending on whether $M^+$ is represented by $K^+$, $Rb^+$ or $Li^+$, $Na^+$, $K^+$ and $Rb^+$ have little decreasing effect on interactions within melts containing $Pb^{2+}$, $Cl^-$ and $Cs^+$, whereas a marked approach to ideal solution behaviour is apparent with $Li^+$ and $Na^+$.

Fig. 3.53 shows the deviations of the partial molar free energies of lead chloride, $\Delta(\Delta \bar{G}_{PbCl_2})$, in the systems (2x $PbCl_2$ + x CsCl) —— (1 - 3x)MCl, from those of the system $PbCl_2$-CsCl, as functions of the ratio (mole fraction MCl)/(mole fraction CsCl). The limits of error are listed in Table 3.62 for each value. In this series, the linear dependence of $\Delta(\Delta \bar{G}_{PbCl_2})$ for each system, on the ratio MCl/CsCl, is more striking than in the series (x $PbCl_2$ + x CsCl) —— (1 - 2x)MCl. This linear relationship seems to indicate that the deviations of the thermodynamic properties of the three component systems from those of the binary system, are fundamentally related to the relative polarizing power (or radii) of the alkali metal ions themselves. Fig. 3.53 also illustrates the great similarity between the properties of $Na^+$ and $Li^+$ ions in their molten mixtures and the validity for the classification of the $M^+$ ions into the two

categories mentioned above.

Such a classification has also been proposed by Ukshe[1] et al., in their investigations of the electric double layer in salt melts. They found that molten halides of alkali metals may be divided into two completely distinct groups (i.e. LiX, NaX and KX, RbX, CsX), according to their influence on the double layer capacitance of a lead electrode.

c) Entropies

The excess partial molar entropies of lead chloride, pertaining to each of the systems $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)MCl$, are summarized in Table 4.23 and are illustrated in fig. 4.16. The values for each composition have been estimated from a plot of $\Delta\bar{S}^E_{PbCl_2}$ versus mole fraction $PbCl_2$. Errors in the tabulated values are of the same order of magnitude and are derived from the same source, as for the values in Table 4.20.

By analogy with the series $(x\ PbCl_2 + x\ CsCl)$ —— $(1 - 2x)MCl$, it is concluded that the general tendency of the excess entropy of $PbCl_2$ to show increasing positive values (relative to the system $PbCl_2$-CsCl) as the mole fraction of $PbCl_2$ is decreased, is due to an increase in the dissociation of complex ions. The increase in numbers of "free" ions, are regarded as contributing to a more disorganised structure. The magnitudes of $\Delta\bar{S}^E_{PbCl_2}$, for the systems $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)LiCl$ and $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)NaCl$,

1. Ukshe, Bukun, Leikis and Frumkin: Electrochim Acta, _9 431 (1964)

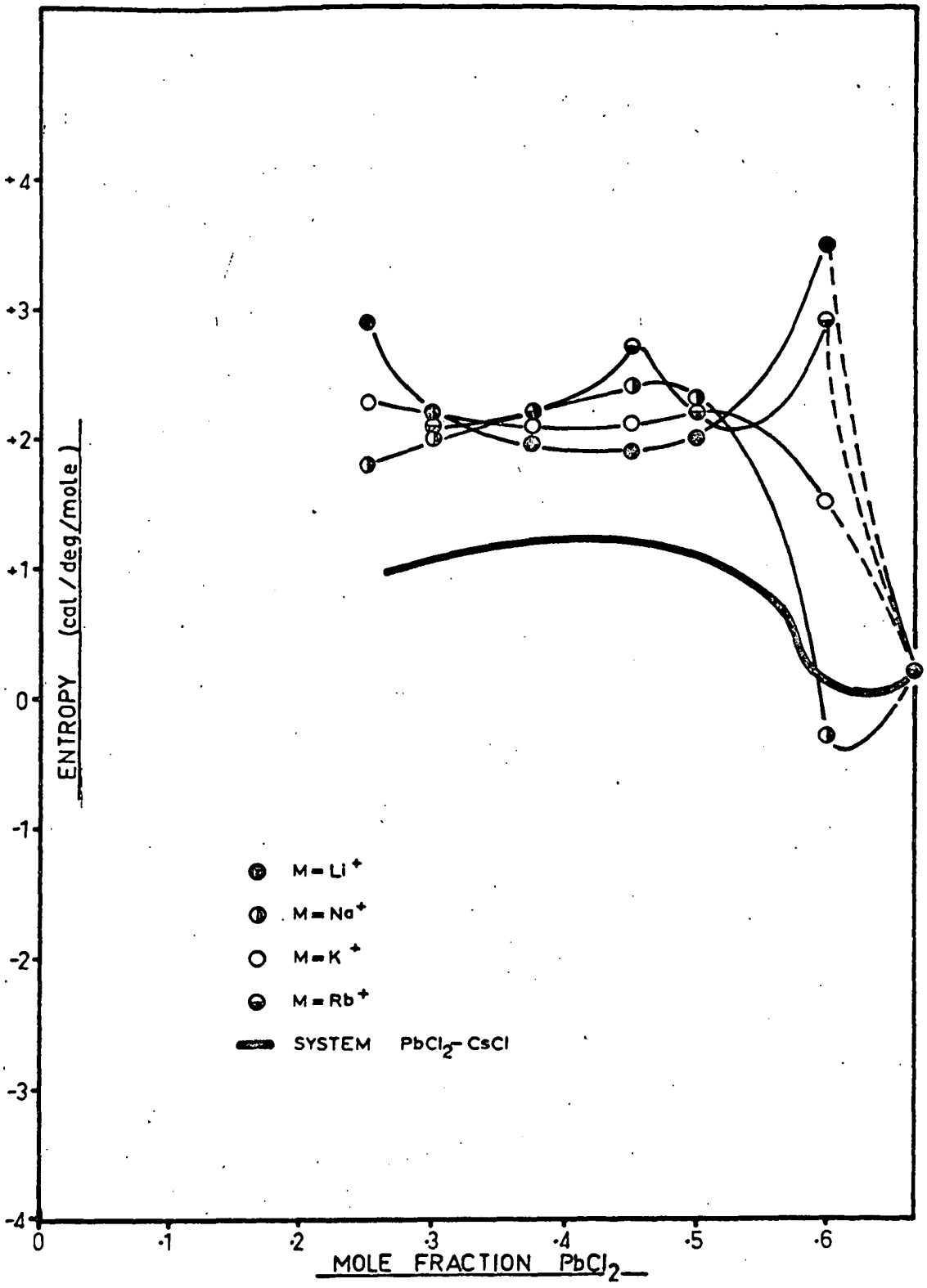



FIG. 4·16

EXCESS PARTIAL ENTROPY OF $PbCl_2$ IN THE SYSTEMS $(2x\,PbCl_2 + x\,CsCl) - (1-3x)\,MCl$ (700°C)

TABLE 4.23

Comparison of the excess partial molar entropies of $PbCl_2$ in the systems $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)MCl$ at 700°C

| m.f. $PbCl_2$ | m.f. CsCl | m.f. MCl | CsCl / MCl | $\Delta\bar{S}_1^E$ (cal/deg/mole), M = | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Cs^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ |
| 0.667 | 0.333 | 0.000 | $\infty$ | 0.20 | - | - | - | - |
| 0.600 | 0.300 | 0.100 | 3.00 | 0.20 | 3.5 | -0.3 | 1.5 | 2.9 |
| 0.500 | 0.250 | 0.250 | 1.00 | 1.10 | 2.0 | 2.3 | 2.2 | 2.2 |
| 0.450 | 0.225 | 0.325 | 0.69 | 1.20 | 1.9 | 2.4 | 2.1 | 2.7 |
| 0.375 | 0.188 | 0.437 | 0.43 | 1.20 | 1.95 | 2.2 | 2.1 | 2.2 |
| 0.300 | 0.150 | 0.550 | 0.27 | 1.20 | 2.2 | 2.0 | 2.2 | 2.1 |
| 0.250 | 0.125 | 0.625 | 0.20 | - | 2.9 | 1.8 | 2.25 | - |

relative to the systems $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)KCl$ and $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)RbCl$, for low concentrations of MCl, are contrary to the tendency expected (compare the series $(x\ PbCl_2 + x\ CsCl)$ —— $(1 - 2x)MCl$.) It would appear that with LiCl, the tendency to break up complex ions outweighs the tendency to decrease the molar volume of the mixture. The reverse is true for NaCl. The errors in $\Delta\bar{S}^E_{PbCl_2}$ are of the order of $\pm$ 0.9 cal/deg/mole but the error associated with the value of $\Delta\bar{S}^E_{PbCl_2}$, for the mixture containing 56 mole % lead chloride in the system with $M^+ = Na^+$, is of the order of $\pm$ 1.8 cal/deg/mole (see Section 3.2). No accurate interpretation of the entropy data can therefore be made, especially in relation to the magnitude of $\Delta\bar{S}^E_{PbCl_2}$ for low concentrations of MCl.

d) Enthalpies

The partial molar enthalpies for the systems (2x $PbCl_2$ + x CsCl) —— (1 - 3x)MCl and $PbCl_2$-CsCl, are summarized in Table 4.24 and are plotted in fig. 4.17. The values at each composition have been estimated from a plot of $\Delta\bar{H}_{PbCl_2}$ versus mole fraction of lead chloride. Errors in these values have similar magnitude to those associated with the enthalpy values for the system (x $PbCl_2$ + x CsCl) —— (1 - 2x)MCl; i.e. of the order 600 cals/mole.

TABLE 4.24

Comparison of the partial molar enthalpies of $PbCl_2$ in the systems (2x $PbCl_2$ + x CsCl) —— (1 - 3x)MCl at 700°C

| m.f. $PbCl_2$ | m.f. CsCl | m.f. MCl | CsCl / MCl | $\Delta\bar{H}_{PbCl_2}$ (K cal/mole), M = | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Cs^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ |
| 0.667 | 0.333 | 0.000 | $\infty$ | -0.45 | - | - | - | - |
| 0.600 | 0.300 | 0.100 | 3.00 | -1.20 | 2.25 | -1.00 | 0.50 | 0.95 |
| 0.500 | 0.250 | 0.250 | 1.00 | -0.66 | 1.20 | 1.00 | 0.75 | 0.35 |
| 0.450 | 0.225 | 0.325 | 0.67 | -1.20 | 1.40 | 1.50 | 0.25 | 0.35 |
| 0.375 | 0.188 | 0.437 | 0.43 | -2.33 | 1.70 | 1.60 | -0.35 | -0.90 |
| 0.300 | 0.150 | 0.550 | 0.27 | -3.20 | 2.25 | 1.40 | -0.75 | -1.95 |
| 0.250 | 0.125 | 0.625 | 0.20 | - | 3.10 | 1.15 | -1.10 | - |

The partial molar enthalpies of lead chloride for all the three-component systems, over the whole range of composition, show more positive values than for the binary system $PbCl_2$-CsCl at corresponding compositions; i.e. for the same mole fractions of $PbCl_2$.

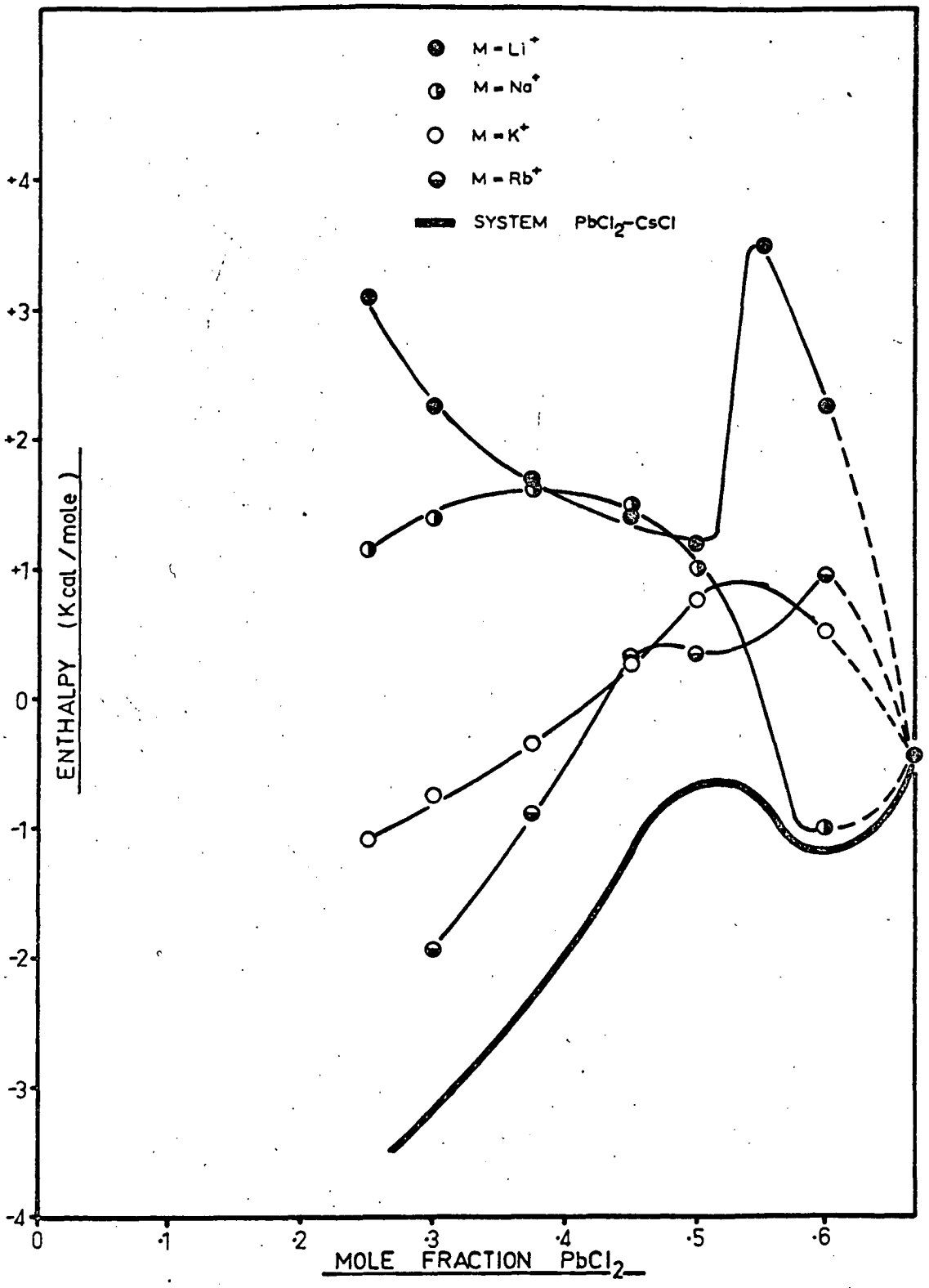



FIG. 4·17 PARTIAL MOLAR ENTHALPIES OF $PbCl_2$ IN THE SYSTEMS $(2xPbCl_2 + xCsCl) — (1-3x)MCl$ (700°C)

This can be explained in terms of the tendency for $M^+$ ions to reduce the stability of complex ions. The degree to which this occurs is evident in mixtures where the ratio CsCl/MCl $< 0.35$. The magnitude of the deviation of $\Delta\bar{H}_{PbCl_2}$ from the value for the system $PbCl_2$-CsCl, then increases in each system as the radius of $M^+$ decreases.

## 4B.4 DERIVATION OF EXPRESSIONS FOR THE ACTIVITY OF LEAD CHLORIDE IN THREE COMPONENT MIXTURES, AS FUNCTIONS OF THE POLARIZING POWER OF THE ALKALI METAL IONS

The correlation between the stability of complex ions of the form $PbCl_n^{(n-2)-}$ and the nature of the polarizing $M^+$ species, has already been discussed. It is proposed that the activity of lead chloride in the three component systems studied, is defined by the two limits of the systems $PbCl_2$-CsCl-MCl; i.e. when the concentration of CsCl = 0 (the system $PbCl_2$-MCl) and the concentration of MCl = 0 (the system $PbCl_2$-CsCl) and by the relative polarizing power of mixtures of ions $M^+$ and $Cs^+$.

Let us assume that the polarizing power, (P), of an alkali metal ion is related to its size by the equation:

$$P \propto 1/r^2, \qquad (4.58)$$

where r is the radius of the ion. The polarizing power, P', relative to that of the $Cs^+$ ion, is given by:

$$P'_{M^+} = P_{M^+}/P_{Cs^+} \qquad (4.59)$$

The relative polarizing power of a mixture of $M^+$ and $Cs^+$ is then given by $P'_{M^+,Cs^+}$, where:

$$P'_{M^+,Cs^+} = (N_{M^+} \cdot P'_{M^+}) + (1 - N_{M^+})P'_{Cs^+} \qquad (4.60)$$

Where $N_{M^+}$ = concentration of $M^+$ ions (in mole fraction units) and

$1 - N_{M^+}$ = concentration of $Cs^+$ ions (in mole fraction units)

The relative polarizing powers of the alkali metal ions are given in Table 4.25.

TABLE 4.25

Relative polarizing powers of the alkali metal ions compared with $Cs^+$

| Alkali metal ion | Ionic radii (r)[1] ($A^o$) | $r^2$ | Polarizing power (P) | Relative polarizing power ($P'_{M^+}$) |
|---|---|---|---|---|
| $Li^+$ | 0.60 | 0.360 | 2.777 | 7.933 |
| $Na^+$ | 0.95 | 0.903 | 1.108 | 3.162 |
| $K^+$ | 1.33 | 1.769 | 0.565 | 1.769 |
| $Rb^+$ | 1.48 | 2.190 | 0.457 | 1.304 |
| $Cs^+$ | 1.69 | 2.856 | 0.350 | 1.000 |

If $P'_{M^+,Cs^+}$ is now plotted against $N_{M^+}/N_{Cs^+}$ ( = M) (see fig. 4.18), then for each experimental concentration of $PbCl_2$, $N_1$, the relative polarizing power of any mixture of the ions $M^+$ and $Cs^+$ can be evaluated (see Table 4.26). Here the value of M is equivalent to the ratio of the true mole fractions of MCl and CsCl in the three component mixture $PbCl_2$-CsCl-MCl.

Consider the system $PbCl_2$-CsCl-MCl. For a given composition, the value of the activity of $PbCl_2$ for this system, is considered to be intermediate between the values of $a_{PbCl_2}$ for the systems $PbCl_2$-CsCl and $PbCl_2$-MCl. The actual magnitude of the activity for a given mole fraction of $PbCl_2$, is assumed to depend on the relative polarizing power of the mixture of $M^+$ and $Cs^+$ ions, at the same composition of lead chloride. Then if:

1. Pauling: Nature of the Chemical Bond, Cornell Univ. Press (1948)

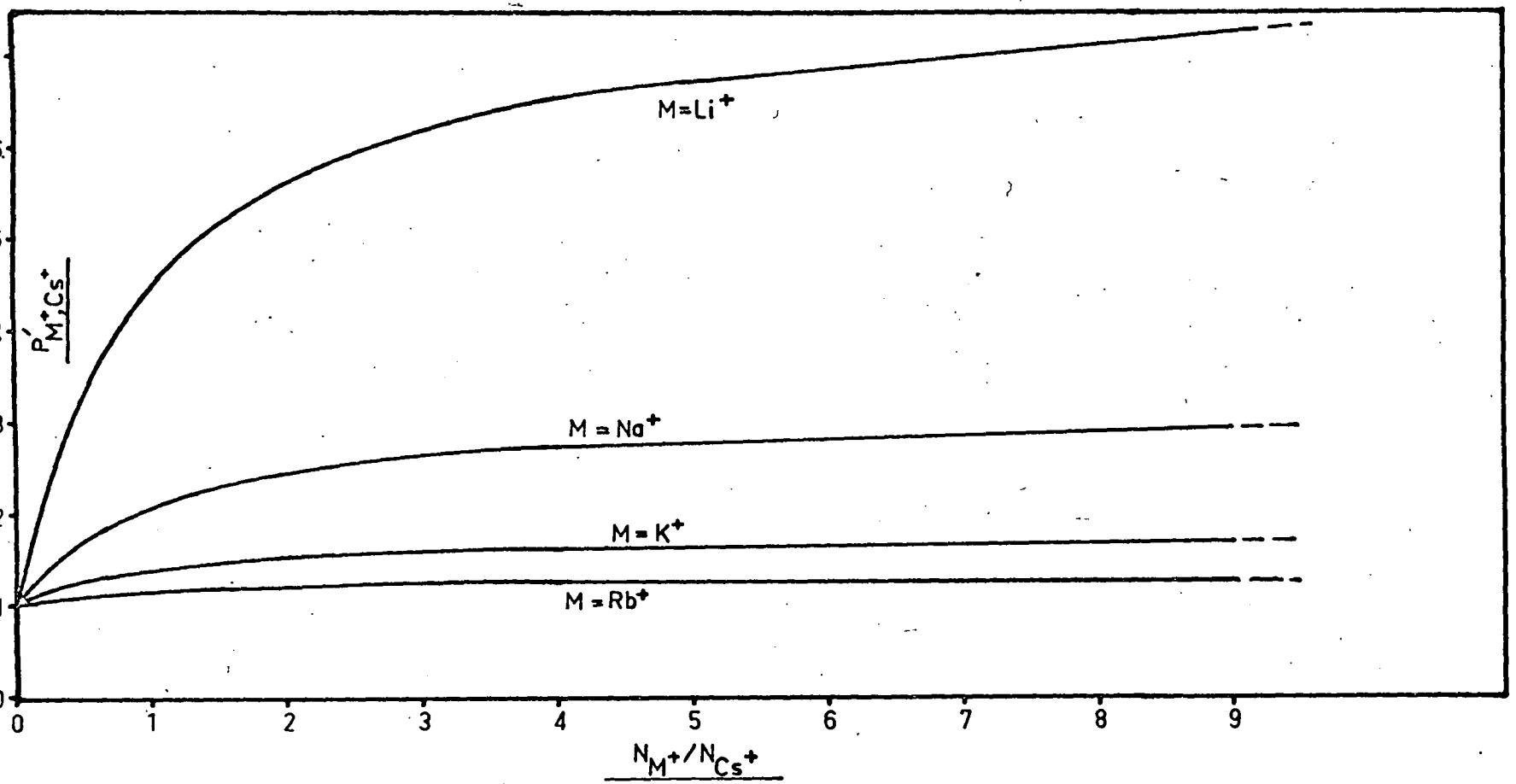



FIG. 4·18

RELATIVE POLARIZING POWERS OF MIXTURES OF THE IONS $M^+$ AND $Cs^+$ (WHERE M = Li, Na, K or Rb) AS A FUNCTION OF THE RATIO $N_{M^+}/N_{Cs^+}$

TABLE 4.26

Relative polarizing powers of mixtures of the ions $Cs^+$ and $M^+$ (where $M^+ = Li^+, Na^+, K^+, Rb^+$)

| $N_{M^+}$ | $N_{Cs^+}$ | $\frac{N_{M^+}}{N_{Cs^+}}$ | $P'_{Li^+,Cs^+}$ | $P'_{Na^+,Cs^+}$ | $P'_{K^+,Cs^+}$ | $P'_{Rb^+,Cs^+}$ |
|---|---|---|---|---|---|---|
| 0.10 | 0.90 | 0.111 | 1.693 | 1.216 | 1.077 | 1.030 |
| 0.20 | 0.80 | 0.250 | 2.386 | 1.432 | 1.154 | 1.061 |
| 0.30 | 0.70 | 0.429 | 3.080 | 1.649 | 1.231 | 1.091 |
| 0.40 | 0.60 | 0.667 | 3.773 | 1.865 | 1.308 | 1.122 |
| 0.50 | 0.50 | 1.000 | 4.467 | 2.081 | 1.385 | 1.152 |
| 0.60 | 0.40 | 1.500 | 5.160 | 2.297 | 1.461 | 1.182 |
| 0.70 | 0.30 | 2.333 | 5.853 | 2.513 | 1.538 | 1.213 |
| 0.80 | 0.20 | 4.000 | 6.546 | 2.730 | 1.615 | 1.243 |
| 0.90 | 0.10 | 9.000 | 7.240 | 2.946 | 1.692 | 1.274 |

$P'_x$ = excess relative polarizing power of the ions $M^+$ and $Cs^+$ above that of $Cs^+$ alone, at a value $N_{M^+}/N_{Cs^+} = M$ and $N_{PbCl_2} = N_1$.

= $P'_{M^+,Cs^+} - 1$;

$P'_x$ (max.) = Maximum excess relative polarizing power of the ions $M^+$ and $Cs^+$ above that of pure $Cs^+$, at a value $N_{M^+}/N_{Cs^+} = M$ and $N_{PbCl_2} = N_1$; here $M = \infty$

= $P'_{M^+} - 1$;

$a'_{PbCl_2}$ = activity of $PbCl_2$ at $N_{PbCl_2} = N_1$ in the binary system $PbCl_2$-CsCl;

$a''_{PbCl_2}$ = activity of $PbCl_2$ at $N_{PbCl_2} = N_1$ in the binary system $PbCl_2$-MCl;

$\Delta a_{PbCl_2}$ = difference between the activities of $PbCl_2$ at corresponding values $N_1$, in the binary systems $PbCl_2$-MCl and $PbCl_2$-CsCl

= $a''_{PbCl_2} - a'_{PbCl_2}$.

The activity of lead chloride in the three component mixtures is then given by:

$$(a_{PbCl_2})_{N_1,M} = \left[ \frac{P'_x}{P'_{x(max.)}} \cdot \Delta a_{PbCl_2} \right] + a'_{PbCl_2} \quad (4.61)$$

Results for the binary systems have been obtained from the work of Lantratov and Alabyshev[1] and Markov, Delimarskii and Panchenko[2], except for the system $PbCl_2$-CsCl which has been investigated in the present work. Although the systems $PbCl_2$-LiCl, $PbCl_2$-NaCl and $PbCl_2$-KCl, were investigated fully by both sets of authors, the results of Lantratov and Alabyshev were preferred as they appeared to be more accurate. Activity results for the system $PbCl_2$-RbCl, were obtained from the data of Markov et al., as they were the only authors to investigate this system. All the activity data used are tabulated in Table 4.27 and plotted in fig. 4.19.

Disadvantages of combining results from this work with that from other sources, lie in the systematic errors present in the measurements of one investigator compared with those of another. Compare for example, the discrepancy in the values of $E^o$, for $PbBr_2$

---

1. Lantratov and Alabyshev: Zhur. Priklad. Khim., 26 263 (1953)
2. Markov, Delimarskii and Panchenko: Zhur. Fiz. Khim., 29 51 (1955)

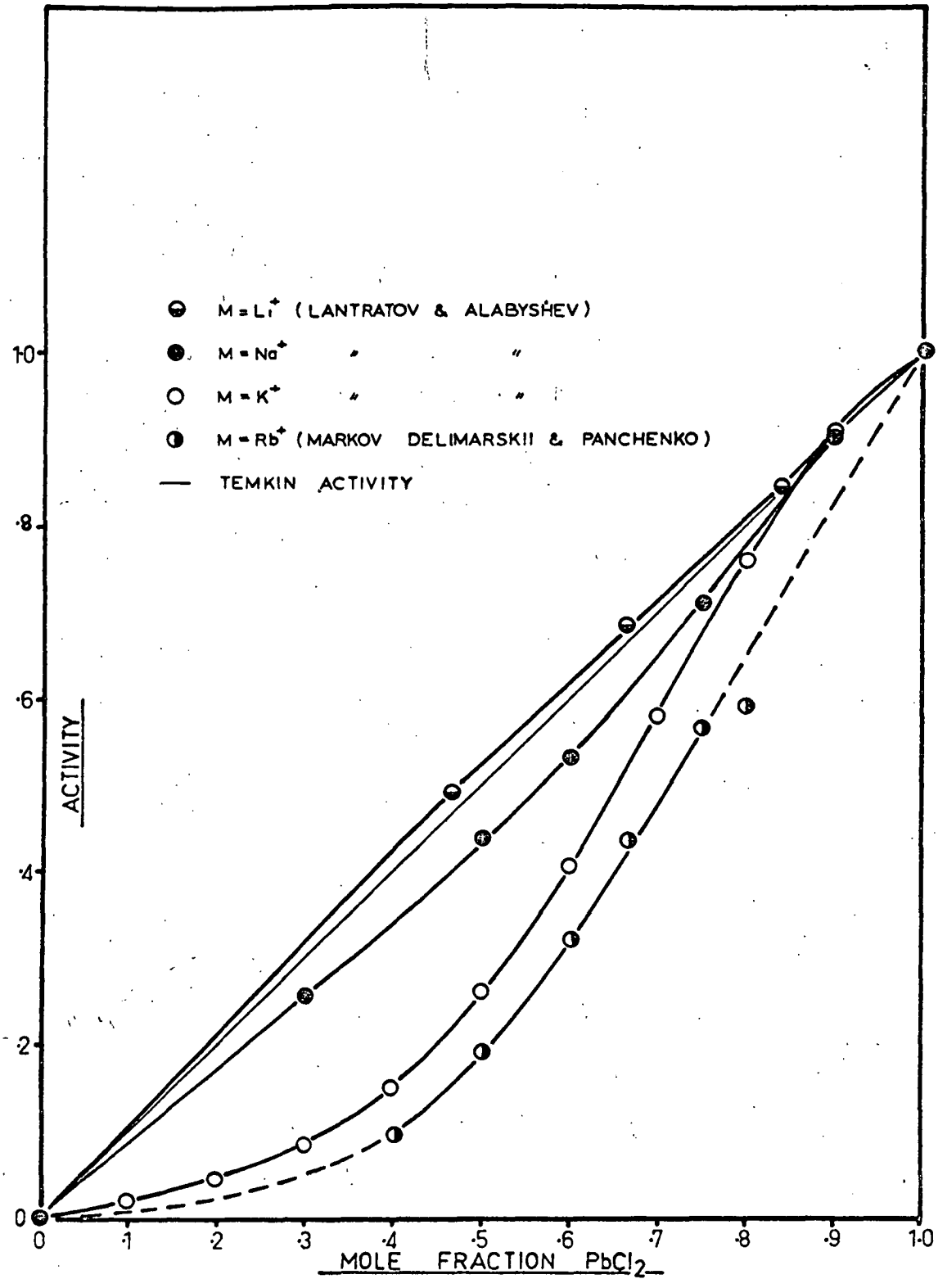



FIG. 4·19

ACTIVITY $PbCl_2$ (700°C) IN THE SYSTEMS $PbCl_2$–MCl FROM RUSSIAN INVESTIGATIONS

TABLE 4.27

The activity of $PbCl_2$ at 700°C in the systems $PbCl_2$-MCl from the work of Lantratov and Alabyshev, and Markov, Delimarskii and Panchenko

| system | $N_1$ | $a_1$ | system | $N_1$ | $a_1$ |
|---|---|---|---|---|---|
| $PbCl_2$-KCl | 0.1 | 0.018 | $PbCl_2$-NaCl | 0.30 | 0.254 |
| | 0.2 | 0.045 | | 0.50 | 0.437 |
| | 0.3 | 0.084 | | 0.60 | 0.532 |
| | 0.4 | 0.150 | | 0.75 | 0.709 |
| | 0.5 | 0.260 | | 0.90 | 0.898 |
| | 0.6 | 0.405 | $PbCl_2$-RbCl | 0.800 | 0.592 |
| | 0.7 | 0.578 | | 0.749 | 0.564 |
| | 0.8 | 0.758 | | 0.667 | 0.434 |
| | 0.9 | 0.907 | | 0.602 | 0.319 |
| $PbCl_2$-LiCl | 0.466 | 0.492 | | 0.502 | 0.193 |
| | 0.663 | 0.684 | | 0.403 | 0.097 |
| | 0.840 | 0.844 | | | |

and $PbCl_2$ (figs. 3.1 and 3.20). Thus, the calculated values for $(a_{PbCl_2})_{N_1,M}$ will have reasonably large errors attached.

Because the activity of lead chloride in the systems $PbCl_2$-CsCl-RbCl is greater than in the system $PbCl_2$-CsCl, the indications are, that as in the binary bromide systems, the 700°C activity isotherm for the system $PbCl_2$-RbCl, will be above that for the system $PbCl_2$-CsCl. The values for $a_{PbCl_2}$ in the $PbCl_2$-RbCl system, obtained by Markov et al., fall below those obtained in the present investigation for $PbCl_2$-CsCl over most of the composition range. Therefore, the theoretical estimation of $(a_{PbCl_2})_{N_1,M}$ using eqn.4.61

TABLE 4.28

Theoretical activities in the systems (x $PbCl_2$ + x CsCl) —— (1 - 2x)MCl at 700°C

| $M^+$ | $N_l$ | $\frac{N_{M^+}}{N_{Cs^+}}$ | $P'_x$ | $a''_{PbCl_2}$ | $a'_{PbCl_2}$ | $\Delta a_{PbCl_2}$ | $\frac{P'_x}{P'_{x(max.)}}$ (= z) | $z.\Delta a_{PbCl_2}$ | $(a_{PbCl_2})_{N_l,M}$ |
|---|---|---|---|---|---|---|---|---|---|
| $Li^+$ | 0.399 | 0.48 | 3.20 | 0.426 | 0.076 | 0.350 | 0.317 | 0.111 | 0.187 |
| | 0.324 | 1.05 | 4.55 | 0.351 | 0.040 | 0.311 | 0.512 | 0.159 | 0.199 |
| | 0.245 | 1.92 | 5.53 | 0.268 | 0.018 | 0.250 | 0.653 | 0.163 | 0.181 |
| | 0.150 | 4.51 | 6.66 | 0.170 | 0.006 | 0.164 | 0.816 | 0.134 | 0.140 |
| $Na^+$ | 0.398 | 0.50 | 1.71 | 0.340 | 0.075 | 0.265 | 0.328 | 0.087 | 0.162 |
| | 0.329 | 1.06 | 2.11 | 0.280 | 0.041 | 0.239 | 0.513 | 0.123 | 0.167 |
| | 0.250 | 1.99 | 2.44 | 0.208 | 0.019 | 0.189 | 0.666 | 0.126 | 0.145 |
| | 0.145 | 4.58 | 2.80 | 0.122 | 0.006 | 0.116 | 0.833 | 0.097 | 0.103 |
| $K^+$ | 0.396 | 0.48 | 1.24 | 0.149 | 0.074 | 0.075 | 0.312 | 0.023 | 0.097 |
| | 0.322 | 1.04 | 1.39 | 0.096 | 0.038 | 0.058 | 0.507 | 0.029 | 0.067 |
| | 0.248 | 2.02 | 1.50 | 0.063 | 0.019 | 0.044 | 0.650 | 0.029 | 0.048 |

## TABLE 4.29

**Theoretical activities in the systems $(2x\ PbCl_2 + x\ CsCl) \longrightarrow (1 - 3x)MCl$ at 700°C**

| $M^+$ | $N_1$ | $\frac{N_{M^+}}{N_{Cs^+}}$ | $P'_x$ | $a''_{PbCl_2}$ | $a'_{PbCl_2}$ | $\Delta a_{PbCl_2}$ | $\frac{P'_x}{P'_{x(max.)}}$ (= z) | $z.\Delta a_{PbCl_2}$ | $(a_{PbCl_2})_{N_1,M}$ |
|---|---|---|---|---|---|---|---|---|---|
| $Li^+$ | 0.551 | 0.596 | 3.56 | 0.576 | 0.275 | 0.301 | 0.369 | 0.111 | 0.386 |
| | 0.491 | 0.959 | 4.38 | 0.515 | 0.185 | 0.330 | 0.488 | 0.161 | 0.346 |
| | 0.418 | 1.840 | 5.46 | 0.445 | 0.095 | 0.350 | 0.643 | 0.225 | 0.320 |
| | 0.322 | 3.023 | 6.21 | 0.348 | 0.038 | 0.310 | 0.751 | 0.233 | 0.271 |
| | 0.250 | 5.168 | 6.80 | 0.273 | 0.020 | 0.253 | 0.837 | 0.212 | 0.232 |
| $Na^+$ | 0.355 | 2.79 | 2.60 | 0.302 | 0.051 | 0.251 | 0.740 | 0.186 | 0.237 |
| | 0.237 | 5.26 | 2.85 | 0.198 | 0.016 | 0.182 | 0.856 | 0.156 | 0.172 |
| | 0.561 | 0.50 | 1.71 | 0.492 | 0.290 | 0.202 | 0.328 | 0.066 | 0.356 |
| | 0.461 | 1.30 | 2.22 | 0.399 | 0.145 | 0.254 | 0.564 | 0.143 | 0.288 |
| $K^+$ | 0.501 | 0.966 | 1.38 | 0.260 | 0.198 | 0.062 | 0.494 | 0.031 | 0.229 |
| | 0.407 | 1.80 | 1.49 | 0.158 | 0.083 | 0.075 | 0.637 | 0.048 | 0.131 |
| | 0.330 | 3.09 | 1.59 | 0.100 | 0.041 | 0.059 | 0.767 | 0.045 | 0.086 |
| | 0.241 | 5.22 | 1.64 | 0.060 | 0.017 | 0.043 | 0.832 | 0.036 | 0.053 |

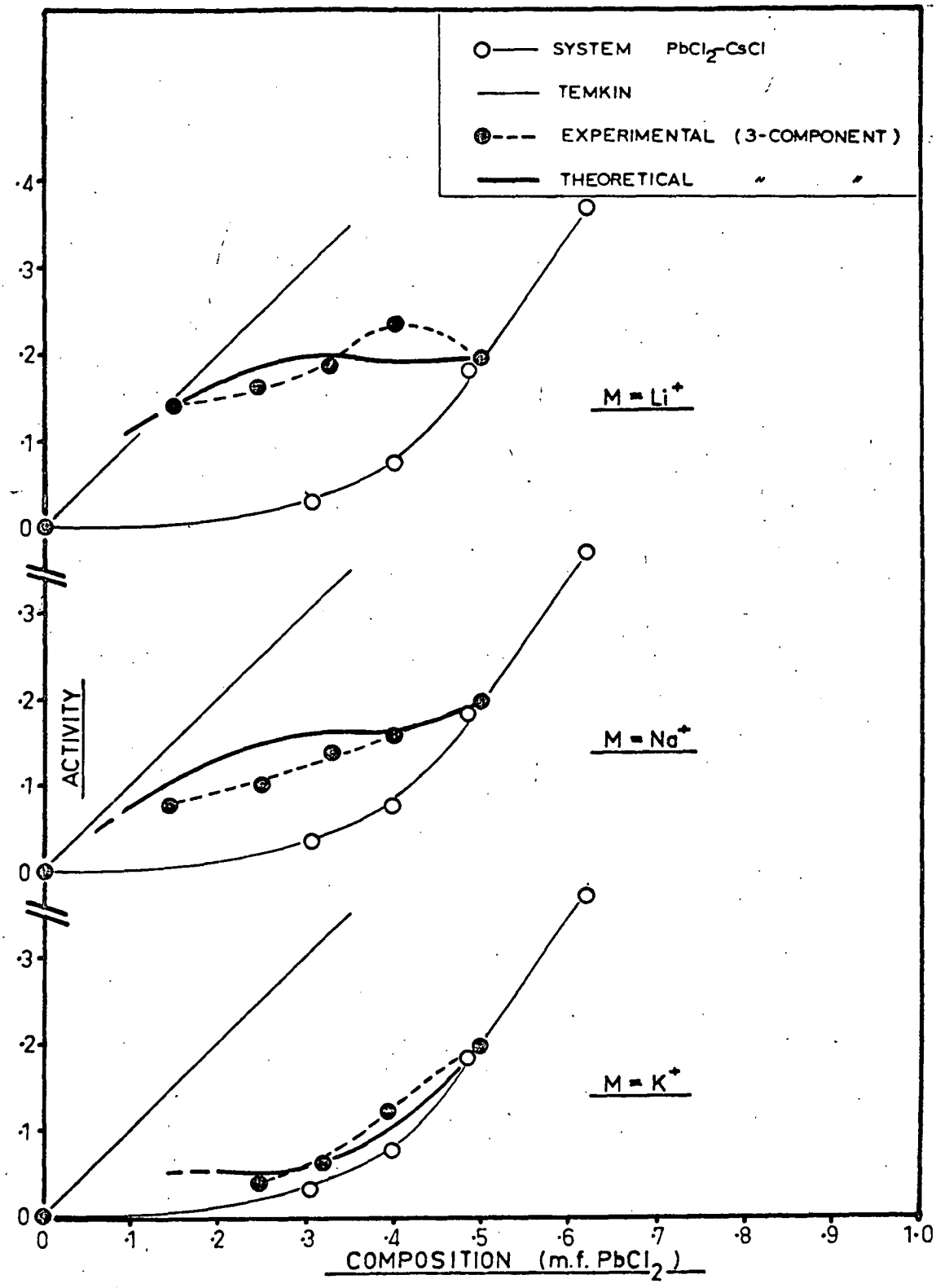



FIG. 4·20

THEORETICAL & EXPTL. ACTIVITIES OF $PbCl_2$ IN THE SYSTEM $(x\,PbCl_2 + x\,CsCl) - (1-2x)MCl$ (700°C)

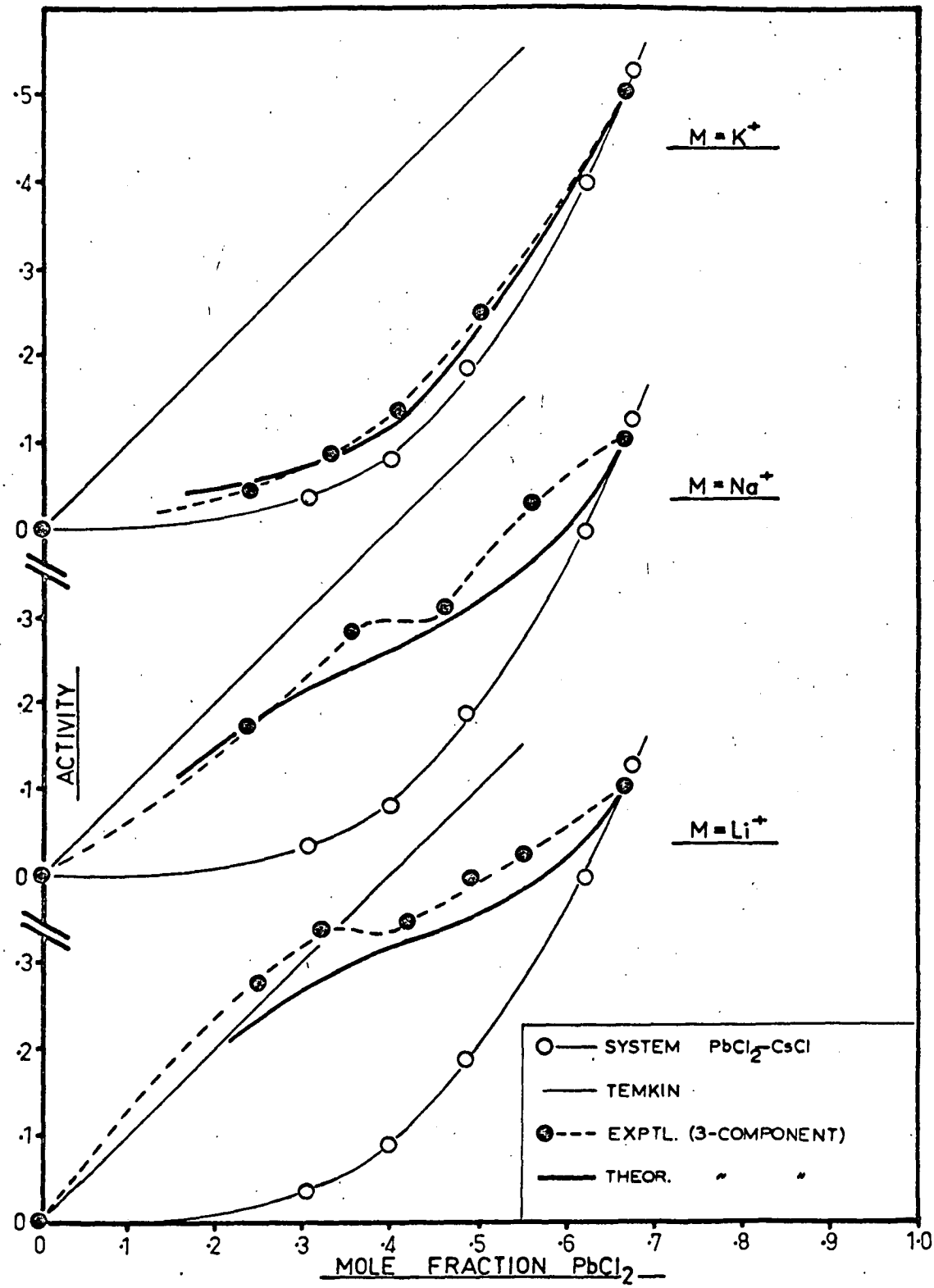



FIG. 4·21 THEORETICAL & EXPTL. ACTIVITIES OF $PbCl_2$ IN THE SYSTEM $(2x\,PbCl_2 + x\,CsCl) - (1-3x)\,MCl$ (700°C)

cannot be accomplished.

Values for $(a_{PbCl_2})_{N_1,M}$, for each of the experimental compositions in the systems $(x\ PbCl_2 + x\ CsCl)$ —— $(1 - 2x)MCl$ and $(2x\ PbCl_2 + x\ CsCl)$ —— $(1 - 3x)MCl$, are listed in Tables 4.28 and 4.29 respectively and are plotted in figs. 4.20 and 4.21 for the cases $M^+ = Li^+$, $Na^+$ and $K^+$.

When the discrepancy between the Russian work and the present work is taken into consideration, reasonable agreement between theoretical and experimental results is obtained. It appears that deviations in the activity of lead chloride from the ideal values in the three component systems studied, are directly related to the polarizing powers of the alkali metal cations in the mixtures.

## SECTION C

## THE RECIPROCAL SYSTEMS

## $Cd^{2+}/Na^{+}/Cl^{-}/Br^{-}$

## 4C.1 GENERAL INTRODUCTION

From the investigations of Van Artsdalen[1] and some Russian workers[2,3], cadmium chloride and to a larger extent cadmium bromide, are regarded as being associated (as $CdX_2$ molecules) in the pure state. Van Artsdalen has evaluated the equilibrium constants (K) for the reactions:

$$AX_2 \overset{K}{\rightleftharpoons} A^{2+} + 2X^-$$

(where $AX_2$ = $PbCl_2$, $CdCl_2$ and $CdBr_2$), for very dilute solutions of $AX_2$ in molten $NaNO_3$. The values obtained for K were: $0.033 \pm 0.005$, $0.0031 \pm 0.0004$, and $0.00035 \pm 0.00011$, for $PbCl_2$, $CdCl_2$ and $CdBr_2$, respectively. The systems $CdCl_2$ + alkali metal chlorides, investigated by Lantratov and Alabyshev[2], show appreciable positive excess chemical potentials (e.g. + 250 cal/mole for the system $CdCl_2$-NaCl, for the mixture containing 0.80 mole fraction $CdCl_2$) for certain compositions and these have been attributed to the presence of undissociated molecules in the standard state of pure $CdCl_2$. In the present investigations of the systems $PbBr_2$ - alkali metal bromides, no correspondingly large positive values for $\Delta\bar{G}_1^E$ are observed. The present author considers therefore, that the extent of the association in the pure cadmium halides is much greater than for the corresponding lead halides.

---

1. Van Artsdalen: J. Phys. Chem., 60 172 (1956)
2. Lantratov and Alabyshev: Zhur. Priklad. Khim., 26 353 (1953)
3. Delimarskii and Markov: Electrochem. of Fused Salts, Sigma Press, (1961)

Consider the following equilibria:

$$CdBr_2 \rightleftharpoons Cd^{2+} + 2Br^- \qquad K = 3.5 \times 10^{-4} \qquad (4.f)$$

$$CdCl_2 \rightleftharpoons Cd^{2+} + 2Cl^- \qquad K = 3.1 \times 10^{-3} \qquad (4.g)$$

If in the cryoscopic investigations of Van Artsdalen[1], it is assumed that the solvent ($NaNO_3$) has no effect on the equilibria 4.f and 4.g, then, from the relative magnitudes of the dissociation constants, it is evident that bromine will replace chlorine in solutions of cadmium chloride and bromide ions, i.e.:

$$CdCl_2 + 2Br^- \rightleftharpoons CdBr_2 + 2Cl^-, \quad K \approx 10 \qquad (4.h)$$

If in a reciprocal cadmium halide, sodium halide mixture, the following exchange reaction is assumed:

$$CdX_2 + 2NaY \rightleftharpoons CdY_2 + 2NaX, \qquad (4.i)$$

(where X is either $Br^-$ or $Cl^-$ and Y either $Cl^-$ or $Br^-$), then cadmium ions will, according to the results of Van Artsdalen, preferentially become associated with bromide ions. Apart from workers such as Lantratov and Shevlyakova[2], who suggest the presence of the species $CdX_6^{4-}$ in mixtures of cadmium and potassium halides, Van Artsdalen[1], Bredig[3] and Ellis et al.[4], infer that the most predominent species in these melts is $CdX_4^{2-}$. Van Artsdalen has evaluated the association constant for cadmium chloride and chloride ions as:

$$CdCl_2 + 2Cl^- \rightleftharpoons CdCl_4^{2-}, \qquad K = 4.4 \qquad (4.j)$$

---


1. Van Artsdalen: J. Phys. Chem., 60 172 (1956)
2. Lantratov and Shevlyakova: J. Appl. Chem., (U.S.S.R.) 34 2433 (1961)
3. Bredig: J. Chem. Phys., 37 451 (1962)
4. Ellis, Smith, Wilcox and Crook: J. Phys. Chem., 65 1186 (1961)

Ellis et al., by consideration of the reciprocal system $CdCl_2$-KBr, have assumed that the association constant for the above reaction will be less than that involving $CdBr_2$ and bromide ions, in which case:

$$CdCl_4^{2-} + 4Br^- \rightleftharpoons CdBr_4^{2-} + 4Cl^-, \quad K > 1 \qquad (4.k)$$

Thus, in the region of complex ion formation, the concentration of free bromide ions will be low, except for mixtures very rich in the alkali bromide. It is therefore likely, that interactions in the system cadmium bromide-alkali metal chloride, will be similar to those involving the corresponding alkali metal bromide.

Consider the equilibrium reaction:

$$CdCl_2 + 2NaBr \rightleftharpoons CdBr_2 + 2NaCl$$

Let $N_1$ and $N_2$ be the mole fractions of $CdCl_2$ and NaBr respectively. Then the mole fractions of $CdCl_2$, NaBr and $CdBr_2$, can vary between the limits 0-1, 1-0 and 0-0.33 mole fraction units, respectively. The maximum stoichiometric concentration of $CdBr_2$ occurs in the mixture containing 0.33 mole fraction $CdCl_2$. As the mole fraction of cadmium bromide either decreases to zero or increases to unity from this value, the mole fraction of $CdBr_2$ will tend to zero. Thus, for each value of the mole fraction of $CdBr_2$, there are two possible mixtures of components, depending on whether NaBr or $CdCl_2$ is in excess in the original mixture. Consider that the above equilibrium reaction lies completely to the right. Then the two cases may be represented as follows:

Excess $CdCl_2$ ($N_1 > 2N_2$)

$$(N_1)CdCl_2 + (N_2)NaBr \longrightarrow (\tfrac{1}{2}N_2)CdBr_2 + (N_1 - \tfrac{1}{2}N_2)CdCl_2 + (N_2)NaCl$$

Excess NaBr ($N_1 < 2N_2$)

$$(N_1)CdCl_2 + (N_2)NaBr \longrightarrow (N_1)CdBr_2 + (N_2 - 2N_1)NaBr + (2N_1)NaCl$$

The interpretation of thermodynamic data for $CdBr_2$ in relation to either the weighed in mole fractions of $CdCl_2$ and NaBr, or to the mole fraction of $CdBr_2$, is considered to be so involved as to be impractical and therefore such quantities will not be discussed.

The same difficulties are not encountered in the system $CdBr_2$-NaCl and hence thermodynamic properties of $CdBr_2$ will be discussed as functions of the mole fraction of $CdBr_2$.

## 4C.2 THE SYSTEM $CdBr_2$-NaCl

### a) Activity of the components

The activity coefficient of $CdBr_2$ and the deviations of the activity of $CdBr_2$ from the Temkin activity in the system $CdBr_2$-NaCl, show very similar tendencies to those for the binary system $CdBr_2$-NaBr (investigated by Lantratov and Shevlyakova[1]) - see Tables 4.30 and 4.31. This supports the earlier statement that the interactions in the two systems may be similar.

TABLE 4.30

Percentage deviations of the activity of $CdBr_2$ from the ideal Temkin values in the system $CdBr_2$-NaCl at 700°C

| m.f. $CdBr_2$ | 0.20 | 0.25 | 0.30 | 0.35 | 0.40 | 0.45 | 0.50 | 0.55 |
|---|---|---|---|---|---|---|---|---|
| $\Delta a_{CdBr_2}$ (%) | 0 | -17.5 | -23 | -21 | -15 | -11 | - 8 | - 7 |
| m.f. $CdBr_2$ | 0.60 | 0.65 | 0.70 | 0.75 | 0.80 | 0.85 | 0.90 | 0.95 |
| $\Delta a_{CdBr_2}$ (%) | - 9 | -10 | - 3 | +30 | +26 | +14 | + 6 | + 1 |

TABLE 4.31

Percentage deviations of the activity of $CdBr_2$ from the ideal Temkin values in the system $CdBr_2$-NaBr at 700°C

| m.f. $CdBr_2$ | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 |
|---|---|---|---|---|---|---|---|---|
| $\Delta a_{CdBr_2}$ (%) | -29 | -26 | -16 | - 3 | + 4 | + 8 | + 8 | + 6 |

1. Lantratov and Shevlyakova: J. Appl. Chem., (U.S.S.R.), 34 2433 (1961)

The initial additions of NaCl to pure $CdBr_2$ are accompanied by a sharp increase in the activity coefficient of cadmium bromide. This can be attributed to the dissociation of cadmium bromide "molecules". The magnitude of $\gamma_{CdBr_2}$ for mixtures rich in $CdBr_2$ is much greater than the magnitudes of $\gamma_{PbBr_2}$ and $\gamma_{PbCl_2}$ in the systems $PbBr_2$-CsBr and $PbCl_2$-CsCl respectively, for corresponding compositions. The difference in magnitude is considered to be due to the greater degree of association in $CdBr_2$ mixtures, compared to the degree of association in the $PbX_2$-CsX mixtures.

For mixtures containing more than 28 mole % NaCl, the tendency to form complex ions becomes greater than the tendency for the dissociation of $CdBr_2$ "molecules" and hence negative deviations of $a_{CdBr_2}$ from the Temkin activity are observed.

Because the polarizing power of the $Na^+$ ion is sufficiently large, the concentration of complex species is relatively small compared to systems such as $PbX_2$-CsX (see for example the systems $PbCl_2$-CsCl-NaCl) and the deviations from the Temkin activity are therefore small. The maximum in activity deviation between 0.3 and 0.35 mole fraction $CdBr_2$ and the minimum in the activity coefficient isotherm in the composition region 0.3-0.4 mole fraction $CdBr_2$, indicate that the greatest interaction occurs in this composition range. The most predominant complex species is therefore presumed to be the ion $CdBr_4^{2-}$.

In the composition range 0-60 mole % $CdBr_2$, the effect of increasing the temperature is to increase the negative deviation from the

Temkin activity. Owing to the presence of the sodium ion, the concentration of complex ions can be assumed to be low (see Section 4A.2a(ii)) and the dissociation of these species due to increased thermal vibration will constitute only a minor effect. The observed temperature effect therefore, is attributed to an increase in ion association in the melt. For mixtures containing between 60 and 100 mole % $CdBr_2$, the predominant effect is an increase in $a_{CdBr_2}$ with increase of temperature. This is to be expected, if, for these compositions, the positive deviation in activity is due to the dissociation of $CdBr_2$ molecules, because an increase in temperature will cause greater dissociation. For this range of composition, the increase in ion pair formation with increase in temperature is evidently a minor effect. For mixtures containing between 80 and 100 mole % $CdBr_2$, the errors in the activity are relatively high compared to the activities at other compositions, so that it is quite conceivable that the reversal of the temperature dependence of $a_{CdBr_2}$ at 0.79 mole fraction $CdBr_2$ is unreal.

b) Free energies

Interpretation of the values of the partial molar free energies of $CdBr_2$ and the integral free energies is difficult because of the lack of knowledge of the excess quantities. The exchange reaction in reciprocal molten salt mixtures gives rise to thermodynamic quantities which differ markedly from those of the corresponding true

binary systems. Blander[1] inter alia, using the theory of conformal ionic mixtures[2], has obtained the following expression for the excess molar Helmholtz free energy of mixing, $\Delta A^{E}_{M}$, of the salts Ac and BD:

$$\Delta A^{E}_{M} = N_A N_D \overset{o}{\Delta A} + N_D \Delta A^{E}_{12} + N_C \Delta A^{E}_{34} + N_A \Delta A^{E}_{13} + N_B \Delta A^{E}_{24} + N_A N_B N_C N_D \Lambda + \ldots\ldots \quad (4.62)$$

where $N_a$ refers to the ion fraction of "a";

" $\overset{o}{\Delta A}$, is the standard molar Helmholtz free energy change for the reaction:

$$AC(liq.) + BD(liq.) \rightleftharpoons AD(liq.) + BC(liq.);$$

" AD, is designated as salt 1, BD as 2, AC as 3 and BC as 4;

" $\Delta A^{E}_{ij}$, is the excess free energy of mixing of the binary mixture of salts i and j, and up to the second order terms is given by:

$$\Delta A^{E}_{12} = N_A N_B \lambda_{12}$$

$$\Delta A^{E}_{13} = N_C N_D \lambda_{13}$$

etc.

where $\lambda_{ij}$, is an energy parameter.

Inability to estimate the energy terms makes such excess quantities inaccessible to calculate. Partial and integral free energies for the system $CdBr_2$-NaCl cannot be compared to those for other binary systems; nor can the magnitude and type of interactions within the melt be estimated.

---

1. Blander and Topol: to be published
2. Blander and Yosim: J. Chem., Phys., 39 2610 (1963)

c) Entropies and Enthalpies

Similar limitations hold for these thermodynamic functions as for the free energies. They will therefore not be discussed.

## 4C.3 THE SYSTEM $CdCl_2$-NaBr

### a) Activity of the components

At both extremes of the concentration scale (mole fraction $CdCl_2$ = 0, 1), the value of $a_{CdBr_2}$ is zero for this system (see fig. 3.63). Although systems such as $PbSO_4$-NaCl[1] and $PbCl_2$-NaBr[2], have shown maxima for $a_{PbBr_2}$ at compositions which are in reasonable agreement with those predicted by the Temkin equation, the present system shows considerable disagreement for $a_{CdBr_2}$. The activity of $CdBr_2$, calculated by both the Temkin and by the Flood et al. models, exhibits a maximum value, when plotted against composition, at the composition corresponding to 25 mole % $CdCl_2$. The experimental maximum however, occurs at about 75 mole % $CdCl_2$. This phenomenon, together with the positive and negative excess activities, can be explained in terms of (a) complex ion formation, and (b) dissociation of the cadmium halide "molecules".

The large value for the activity coefficient of cadmium bromide and consequently the large positive deviation of $a_{CdBr_2}$ from the Temkin activity, is possibly due to the dissociation of $CdCl_2$ "molecules" (or $CdBr_2$ "molecules" formed according to reaction 4.h), on the addition of $Na^+$ ions. This causes an increase in the ion fractions of $Cd^{2+}$ and $Br^-$ and hence gives rise to a larger value for the activity of $CdBr_2$. The magnitude of this deviation compared to that for the

---

1. Bloom and Welch: Trans. Faraday Soc., 57 61 (1961)
2. Bloom and Welch: Trans. Faraday Soc., 59 410 (1963)

system $CdBr_2$-NaCl is rather puzzling and no satisfactory explanation can be offered. As the mole fraction of sodium bromide increases, so the tendency to form complex species is increased, resulting finally, in a negative deviation in the activity for mixtures containing more than 58 mole % NaBr. Although the nature of the species cannot be ascertained from these measurements, it is possible that these deviations are due to the complex ions $CdBr_4^{2-}$ and perhaps $CdCl_4^{2-}$, which previous workers have assumed to be present in binary cadmium halide-alkali metal halide melts (see Section 4C.1).

Assuming the dissociation of cadmium halide molecules with initial additions of $Na^+$ to predominate over the tendency to form complex ions, an increase in temperature would be expected to cause an increase in the activity of $CdBr_2$ (as in the previous system). This is observed experimentally in the region of the positive excess activity. In the composition region in which the negative excess activity of $CdBr_2$ pertains, a decrease in the activity of $CdBr_2$ with increase in temperature is observed. This phenomenon can be interpreted in the same way as for the system $CdBr_2$-NaCl.

b) <u>Free energies, entropies and enthalpies</u>

These thermodynamic functions will not be discussed for the reasons already mentioned (see Section 4C.1).

## 4C.4 ACTIVITY MODELS FOR THE SYSTEMS $CdBr_2$-NaCl AND $CdCl_2$-NaBr

a) Temkin and Flood, Førland and Grjotheim models*

For the systems $CdBr_2$-NaCl and $CdCl_2$-NaBr, both the Temkin and the Flood et al. models predict activities of cadmium bromide which are different in magnitude to those observed experimentally - see Tables 4.32 and 4.33.

TABLE 4.32

System $CdBr_2$-NaCl

Comparison of the Temkin and Flood et al. activities for $CdBr_2$, with those obtained experimentally (values interpolated from fig.3.57 - 700°C)

| mole fraction $CdBr_2$ | $a_{CdBr_2}$ | | |
|---|---|---|---|
| | Temkin | Flood et al. | Observed |
| 0.00 | 0.0000 | 0.0000 | 0.000 |
| 0.10 | 0.0023 | 0.0060 | 0.003 |
| 0.20 | 0.0223 | 0.0370 | 0.019 |
| 0.30 | 0.0640 | 0.0983 | 0.050 |
| 0.40 | 0.1304 | 0.1866 | 0.108 |
| 0.50 | 0.2225 | 0.2963 | 0.207 |
| 0.60 | 0.3375 | 0.4218 | 0.319 |
| 0.70 | 0.4753 | 0.5585 | 0.453 |
| 0.80 | 0.6322 | 0.7023 | 0.784 |
| 0.90 | 0.8071 | 0.8501 | 0.860 |
| 1.00 | 1.0000 | 1.0000 | 1.000 |

* See Section 1.5b

TABLE 4.33

System $CdCl_2$-NaBr
Comparison of the Temkin and Flood et al. activities for $CdBr_2$, with those obtained experimentally (values interpolated from fig. 3.63 - 700°C)

| mole fraction $CdCl_2$ | $a_{CdBr_2}$ | | |
|---|---|---|---|
| | Temkin | Flood et al. | Observed |
| 0.00 | 0.0000 | 0.0000 | 0.000 |
| 0.10 | 0.0669 | 0.1217 | 0.015 |
| 0.20 | 0.0890 | 0.1481 | 0.0315 |
| 0.30 | 0.0868 | 0.1338 | 0.049 |
| 0.40 | 0.0736 | 0.1050 | 0.066 |
| 0.50 | 0.0555 | 0.0741 | 0.082 |
| 0.60 | 0.0375 | 0.0469 | 0.094 |
| 0.70 | 0.0217 | 0.0257 | 0.1015 |
| 0.80 | 0.0099 | 0.0110 | 0.102 |
| 0.90 | 0.0025 | 0.0026 | 0.087 |
| 1.00 | 0.0000 | 0.0000 | 0.000 |

The discrepancy between experimental and theoretical activities, has been explained in terms of interactions within the melt which are not present in the hypothetical solution for which the Temkin equation is valid. It has been proposed that these interactions result in complex ion formation which reduce the numbers of "free" $Cd^{2+}$ and $Br^-$ ions.

b) Welch model

To explain the deviations of the observed activity of $PbBr_2$ from that predicted by Temkin for the reciprocal systems $Pb^{2+}/Na^+/Br^-/Cl^-$,

Welch[1] proposed that the formation of PbClBr as well as $PbBr_2$ was an integral part of the cell reaction. He considered three possible reactions for the formation of the binary lead halide, i.e.:

1. $Pb \longrightarrow Pb^{2+} + 2e^-$

   $Br_2 + 2e^- \longrightarrow 2Br^-$

   ---

   $Pb + Br_2 \longrightarrow PbBr_2$

2. $Pb \longrightarrow Pb^{2+} + 2e^-$

   $Pb^{2+} + Cl^- \longrightarrow PbCl^+$

   $Br_2 + 2e^- \longrightarrow 2Br^-$

   $PbCl^+ + Br^- \longrightarrow PbClBr$

   ---

   $Pb + Br_2 + Cl^- \longrightarrow PbClBr + Br^-$

3. $Pb \longrightarrow Pb^{2+} + 2e^-$

   $Br_2 + 2e^- \longrightarrow 2Br^-$

   $Pb^{2+} + Br^- \longrightarrow PbBr^+$

   $PbBr^+ + Cl^- \longrightarrow PbBrCl$

   ---

   $Pb + Br_2 + Cl^- \longrightarrow PbBrCl + Br^-$

The total free energy change must therefore include terms for both $PbBr_2$ and PbBrCl. Hence the activity will be given by:

$$a_{PbBr_2} = a_{PbBr_2} + \tfrac{1}{2}a_{PbBrCl} + \tfrac{1}{2}a_{PbClBr}$$

$$= a_{PbBr_2} + a_{PbBrCl} \qquad (4.63)$$

(if the method of formation of PbBrCl is assumed to be the same as that for PbClBr)

---

1. Welch: Ph.D. Thesis, University of New Zealand (1960)

Hence if $N_i$ represents the ion fraction of species i etc., then:

$$a_{PbBr_2} = N_{Pb^{2+}} \cdot (N_{Br^-})^2 + N_{Pb^{2+}} \cdot N_{Br^-} \cdot N_{Cl^-}$$
$$= N_{Pb^{2+}} \cdot N_{Br^-} \qquad (4.64)$$
$$\text{(since } N_{Br^-} + N_{Cl^-} = 1)$$

(compare the Temkin definition, $a_{PbBr_2} = N_{Pb^{2+}} \cdot (N_{Br^-})^2$)

Eqn. 4.64 gives good agreement with the experimental values for the reciprocal lead systems.

When applied to the reciprocal cadmium systems however, agreement is poor. The fact that the term $N_{Br^-}$ is not squared, produces activities in excess of those predicted by the Temkin equation and hence gives rise to greater positive excess activities compared to the experimental values.

c) Bloom and Welch model[1,2]

Consider the reaction:

$$A_1X_1 + A_2X_2 \rightleftharpoons A_1X_2 + A_2X_1$$

Then at equilibrium:

$$\frac{a_{A_1X_2} \cdot a_{A_2X_1}}{a_{A_1X_1} \cdot a_{A_2X_2}} = \exp.(-\Delta G/RT) \qquad (4.65)$$

If it is assumed that the ideal entropy of mixing is that defined by Temkin, then:

$$a_{A_1X_1} = a'_{A_1X_1} \cdot \gamma_{A_1X_1} \qquad (4.66)$$

where $a'_{A_1X_1}$, is the ideal Temkin activity of $A_1X_1$ and $\gamma_{A_1X_1}$, is the activity coefficient of $A_1X_1$.

---

1. Bloom and Welch: Disc. Faraday Soc., 32 115 (1961)
2. Bloom and Welch: Trans. Faraday Soc., 59 410 (1963)

In place of eqn. 4.65 therefore, we can write:

$$\frac{\gamma_{A_1X_1} \cdot \gamma_{A_2X_2}}{\gamma_{A_1X_2} \cdot \gamma_{A_2X_1}} = \exp.\ (\Delta G/RT) \qquad (4.67)$$

From eqn. 4.67 and the Gibbs-Duhem relationship, we have:

$$\ln \gamma_{A_1X_1} = \int_{N_{A_1X_1}=1}^{N_{A_1X_1}=N_{A_1X_1}} (N_{A_2X_2}/N_{A_1X_1})\, d \ln \gamma_{A_2X_2} \qquad (4.68)$$

where $N_{A_1X_1}$ is the original mole fraction of $A_1X_1$ added and $N_{A_2X_2}$ ($= 1 - N_{A_1X_1}$), is the original mole fraction of $A_2X_2$. Flood et al., have shown from considerations of bond energies, that molten salts cannot be treated as ideal. They assumed that the deviations from ideality for reciprocal salt systems could be attributed to the interaction of nearest neighbours(1,2). If these solutions are assumed to be regular, then the activity of component $M_1A_1$ in a reciprocal molten salt mixture is given by:

$$a_{M_1A_1} = N_{M_1^+} \cdot N_{A_1^-} \cdot \gamma_{M_1^+} \cdot \gamma_{A_1^-} \times \exp. \sum \left[ N'_{M_1^+} \cdot N'_{A_j^-} \left( \Delta G_{ij}/RT \right) \right] \qquad (4.69)$$

where $\Delta G_{ij}$ is the change in Gibbs free energy for the reaction of one mole of $M_1A_1$ with an equivalent of $M_iA_j$ and where $\sum$, denotes that the contributions from all oppositely charged pairs must be considered. Flood et al., assumed that $\gamma_{M_1^+}$, etc. = 1 and that deviations from the ideal value were due to differences in bond energies between components in the mixture.

---

1. Bloom and Welch: Trans. Faraday Soc., 59 410 (1963)

2. Flood, Førland and Grjotheim: Z. anorg. u allgem. Chem., 276 289 (1954)

Eqn. 4.69 may be rewritten as:

$$\gamma_{A_1X_1} = \exp.\left[\sum N'_{A_i^+} \cdot N'_{X_j^-} \cdot G_{ij}/RT\right] \qquad (4.70)$$

where $N'_{A_i^+}$ and $N'_{X_j^-}$, are cation and anion equivalent fractions of the cations $A_i^+$ and anions $X_j^-$, respectively. They further showed that the contributions to the activity coefficient from interactions other than those from between ions of like sign were negligible.

In the regular solution model of Flood et al., the free energy of mixing, $\Delta G_{ij}$, is assumed to be entirely due to the exchange reaction. Hildebrand and Salstrom[1,2], have shown from considerations of systems such as $A_1X_1$- $A_2X_1$, that although no exchange reaction can take place because of the common ion, there is in fact a partial molar free energy change due to the mixing of ions of like sign to form regular solutions.

Thus in the system $A_1X_1$- $A_2X_1$:

$$RT \ln \gamma_{A_1^+} = b(N_{A_2^+})^2, \qquad (4.71)$$

and in the system $A_1X_1$ - $A_1X_2$:

$$RT \ln \gamma_{X_1^-} = b' (N_{X_2^-})^2. \qquad (4.72)$$

Thus in a molten salt solution containing two different cations $A_1^+$, $A_2^+$ and two different anions $X_1^-$, $X_2^-$, eqn. 4.70 may be modified using 4.71 and 4.72, i.e.:

$$\gamma_{A_1X_1} = \exp.\ (\Delta G\, N'_{A_2^+} \cdot N'_{X_2^-} + b\,(N_{A_2^+})^2 + b'\,(N_{X_2^-})^2)/RT, \qquad (4.73)$$

where b and b', are constants for the regular heat of mixing of cations and anions respectively. Eqn. 4.73 has been used successfully by Bloom and Welch, to calculate $a_{PbBr_2}$ in the reciprocal systems

---

1. Bloom and Welch: Discuss. Faraday Soc., 32 115 (1961)
2. Hildebrand and Salstrom: J. Am. Chem. Soc., 54 4257 (1932)

$Pb^{2+}/Na^{+}/Br^{-}/Cl^{-}$.

Consider the reciprocal molten salt mixture $Cd^{2+}/Na^{+}/Br^{-}/Cl^{-}$. Then the exchange reactions theoretically possible for $CdBr_2$ are:

$$CdBr_2 + 2NaCl \rightleftharpoons CdCl_2 + 2NaBr \qquad \Delta G_1$$

$$CdBr_2 + NaCl \rightleftharpoons CdBrCl + NaBr \qquad \Delta G_2$$

From eqn. 4.70:

$$\gamma_{CdBr_2} = \exp.\ (N'_{Na^+} \cdot N'_{Cl^-} \cdot \Delta G_1/RT + N'_{Na^+} \cdot N'_{Cl^-} \cdot \Delta G_2/RT)$$

$$= \exp.\ (N'_{Na^+} \cdot N'_{Cl^-}/RT\ (\Delta G_1 + \Delta G_2)) \qquad (4.74)$$

Taking into account the heats of mixing $Na^+$ with $Cd^{2+}$ and $Cl^-$ with $Br^-$ we obtain:

$$\gamma_{CdBr_2} = \frac{\exp.\ ((\Delta G_1 + \Delta G_2)\ N'_{Na^+} \cdot N'_{Cl^-} + b\ (N_{Na^+})^2 + 2b'\ (N_{Cl^-})^2)}{RT}$$

If $\Delta G$ is set equal to $(\Delta G_1 + \Delta G_2)$ and the equation rearranged, then:

$$RT \ln \gamma_{CdBr_2} = (\Delta G \cdot N'_{Na^+} \cdot N'_{Cl^-}) + b\ (N_{Na^+})^2 + 2b'\ (N_{Cl^-})^2 \qquad (4.75)$$

where

$$N'_{Na^+} = N_{Na^+}/(1 + N_{Cd^{2+}})$$

$$N'_{Cl^-} = N_{Cl^-} \qquad (4.76)$$

<u>The system $CdCl_2$-NaBr</u>

Using eqn. 4.75 in conjunction with eqn. 4.76, we have:

$$N'_{Na^+} = \frac{N_{Na^+}}{1 + N_{Cd^{2+}}} = \frac{1 - N_{Cd^{2+}}}{1 + N_{Cd^{2+}}}$$

$$N'_{Cl^-} = N_{Cl^-} = \frac{2N_{Cd^{2+}}}{2N_{Cd^{2+}} + N_{Na^+}}$$

$$= \frac{2N_{Cd^{2+}}}{2N_{Cd^{2+}} + N'_{Na^{+}}\,(1 + N_{Cd^{2+}})} \qquad \text{(from 4.76)}$$

$$= \frac{2N_{Cd^{2+}}}{2N_{Cd^{2+}} + \dfrac{(1 - N_{Cd^{2+}})(1 + N_{Cd^{2+}})}{(1 + N_{Cd^{2+}})}}$$

$$= \frac{2N_{Cd^{2+}}}{1 + N_{Cd^{2+}}}$$

and hence:

$$RT \ln \gamma_{CdBr_2} = 2\,\triangle G\,(N_{Cd^{2+}})(1 - N_{Cd^{2+}})/(1 + N_{Cd^{2+}})^2 + b\,(1 - N_{Cd^{2+}})^2 + 8b'\,(N_{Cd^{2+}})^2/(1 + N_{Cd^{2+}})^2 \qquad (4.77)$$

In the limit:

$$N_{Cd^{2+}} = 0, \quad RT \ln \gamma_{CdBr_2} = b \qquad (4.78)$$

$$N_{Cd^{2+}} = 1, \quad RT \ln \gamma_{CdBr_2} = 2b' \qquad (4.79)$$

<u>The system $CdBr_2$-NaCl</u>

Dividing eqn. 4.75 by $N'_{Na^{+}} \cdot N'_{Cl^{-}}$, we have:

$$\frac{RT \ln \gamma_{CdBr_2}}{N'_{Na^{+}} \cdot N'_{Cl^{-}}} = \triangle G + b\,\frac{N_{Na^{+}}\,(1 + N_{Cd^{2+}})}{N_{Cl^{-}}} + 2b'\,\frac{N_{Cl^{-}}}{N'_{Na^{+}}} \qquad (4.80)$$

Now

$$\frac{N_{Na^{+}}\,(1 + N_{Cd^{2+}})}{N_{Cl^{-}}} = \frac{N'_{Na^{+}}\,(1 + N_{Cd^{2+}})^2}{N_{Cl^{-}}}$$

$$N_{Cl^{-}} = \frac{1 - N_{Cd^{2+}}}{1 - N_{Cd^{2+}} + 2N_{Cd^{2+}}}$$

$$N'_{Na^{+}} = \frac{1 - N_{Cd^{2+}}}{1 - N_{Cd^{2+}} + 2N_{Cd^{2+}}}$$

$$\therefore \quad \frac{N'_{Na^+}}{N_{Cl^-}} = 1 \qquad (4.81)$$

and $$\frac{N_{Na^+}\,(1 + N_{Cd^{2+}})}{N_{Cl^-}} = (1 + N_{Cd^{2+}})^2 \qquad (4.82)$$

Substituting 4.81 and 4.82 in 4.80, we have:

$$RT \ln \gamma_{CdBr_2}/N'_{Na^+} \cdot N'_{Cl^-} = \Delta G + 2b' + b\,(1 + N_{Cd^{2+}})^2 \qquad (4.83)$$

In the limit:

$$N_{Cd^{2+}} = 0, \quad RT \ln \gamma_{CdBr_2}/N'_{Na^+} \cdot N'_{Cl^-} = \Delta G + 2b' + b \qquad (4.84)$$

$$N_{Cd^{2+}} = 1, \quad RT \ln \gamma_{CdBr_2}/N'_{Na^+} \cdot N'_{Cl^-} = \Delta G + 2b' = 4b \qquad (4.85)$$

Therefore in the system $CdCl_2$-NaBr, b and b' may be evaluated from extrapolation to $N_{CdCl_2} = 1, 0$ of the plot $RT \ln \gamma_{CdBr_2}$ versus $N_{CdCl_2}$ and for the system $CdBr_2$-NaCl, b and b' may be evaluated by extrapolation to $N_{CdBr_2} = 1, 0$ of the plot $RT \ln \gamma_{CdBr_2}/N'_{Na^+} \cdot N'_{Cl^-}$ versus $N_{CdBr_2}$. On substituting the values of b and b' in eqns. 4.78, 4.79, 4.84, 8.85, $\Delta G$ can be evaluated. The activity of cadmium bromide can then be calculated using eqn. 4.75.

This model was found to be unsatisfactory for the cadmium systems, because (a) extrapolation of the plots for the functions $RT \ln \gamma_{CdBr_2}$ versus $N_{CdCl_2}$ and $RT \ln \gamma_{CdBr_2}/N'_{Na^+} \cdot N'_{Cl^-}$ versus $N_{CdBr_2}$ to the limits $N_{CdX_2} = 0, 1$, for the systems $CdCl_2$-NaBr and $CdBr_2$-NaCl were far too inaccurate, owing to the scatter of the values, and (b) this regular solution approach involving interactions between ions of like sign, produces activities in excess of those predicted by the Temkin model. These deviations are contrary to the observed

negative deviations from the Temkin activity for most compositions. The Bloom and Welch model therefore predicts activities for $CdBr_2$ that are inconsistent with the experimental values of $a_{CdBr_2}$ in both systems.

d) Proposed model

The following expressions for the activity of cadmium bromide have been deduced, assuming an equilibrium between complex cadmium halide ions, cadmium ions and halide ions. Of the complex species theoretically possible, only the four co-ordinated $CdX_4^{2-}$ ions have been considered, because from previous investigations of binary cadmium halide, alkali metal halide systems they appear to be the most predominant species (see Section 4C.1). Since two different species of halide ions are present in these mixtures, then theoretically, the stoichiometry of any one complex can vary between $CdCl_4^{2-}$ and $CdBr_4^{2-}$, with the resulting possibilities: $CdBr_4^{2-}$, $CdBr_3Cl^{2-}$, $CdBr_2Cl_2^{2-}$, $CdBrCl_3^{2-}$, $CdCl_4^{2-}$. From the previous discussion regarding the relative stability of the ions $CdBr_4^{2-}$ and $CdCl_4^{2-}$, it is probable that the dominant species is $CdBr_4^{2-}$. Whether mixed halide complexes do in fact exist is unproven. However, activities will be estimated from the dissociation schemes of all the above $CdX_4^{2-}$ species, in an attempt to explain the experimental results.

For both systems $CdBr_2$-NaCl and $CdCl_2$-NaBr, values for $\alpha$, the degree of dissociation of each complex ion, have been estimated at a composition reference point, by a trial and error procedure.

Subsequent determinations of $a_{CdBr_2}$ have been accomplished by the substitution of this value in the appropriate activity equation.

In the following expressions, let $N_1$ be the original concentration, in mole fraction units, of the cadmium halide species and $N_2$ the concentration of the other component. Let $n_i$ be the number of ions of species i present at equilibrium and let $N_i$ be the ion fraction of i.

(i) The system $CdBr_2$-NaCl

1. The complex $CdBr_4^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdBr_4^{2-} \rightleftharpoons Cd^{2+} + 4Br^-$$

The following calculations apply over the whole composition range.

At equilibrium:

$$n_{Cd^{2+}} = \tfrac{1}{2}N_1 + \tfrac{1}{2}N_1\alpha$$

$$n_{Br^-} = 2N_1\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2$$

$$n_{CdBr_4^{2-}} = \tfrac{1}{2}N_1(1-\alpha)$$

$$N_{Cd^{2+}} = \frac{\tfrac{1}{2}N_1 + \tfrac{1}{2}N_1\alpha}{\tfrac{1}{2}N_1 + \tfrac{1}{2}N_1\alpha + N_2} = \frac{N_1(1+\alpha)}{N_1(1+\alpha) + 2N_2}$$

$$N_{Br^-} = \frac{2N_1\alpha}{2N_1\alpha + N_2 + \tfrac{1}{2}N_1 - \tfrac{1}{2}N_1\alpha} = \frac{4N_1\alpha}{N_1(3\alpha+1) + 2N_2}$$

$$a_{CdBr_2} = \frac{N_1(1+\alpha)}{N_1(1+\alpha) + 2N_2}\left[\frac{4N_1\alpha}{N_1(3\alpha+1) + 2N_2}\right]^2 \qquad (4.86)$$

## 2. The complex $CdBr_3Cl^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdBr_3Cl^{2-} \rightleftharpoons Cd^{2+} + 3Br^- + Cl^-$$

**Case 1.** $2N_1 \leq 3N_2$

At equilibrium:

$$n_{Cd^{2+}} = {}^1/_{3N_1} + {}^2/_{3N_1}\alpha$$

$$n_{Br^-} = 2N_1\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2 - {}^2/_{3N_1} + {}^2/_{3N_1}\alpha$$

$$n_{CdBr_3Cl^{2-}} = {}^2/_{3N_1}\,(1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{{}^1/_{3N_1} + {}^2/_{3N_1}\alpha}{{}^1/_{3N_1} + {}^2/_{3N_1}\alpha + N_2} = \frac{N_1\,(1 + 2\alpha)}{N_1\,(1 + 2\alpha) + 3N_2}$$

$$N_{Br^-} = \frac{2N_1\alpha}{2N_1\alpha + N_2}$$

$$a_{CdBr_2} = \frac{N_1\,(1 + 2\alpha)}{N_1\,(1 + 2\alpha) + 3N_2}\left[\frac{2N_1\alpha}{2N_1\alpha + N_2}\right]^2 \qquad (4.87)$$

**Case 2.** $2N_1 > 3N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1 - N_2 + N_2\alpha$$

$$n_{Br^-} = 2N_1 - 3N_2 + 3N_2\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2\alpha$$

$$n_{CdBr_3Cl^{2-}} = N_2\,(1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1 - N_2 + N_2\alpha}{N_1 - N_2 + N_2\alpha + N_2} = \frac{N_2(\alpha - 1) + N_1}{N_2\alpha + N_1}$$

$$N_{Br^-} = \frac{2N_1 - 3N_2 + 3N_2\alpha}{2N_1 - 3N_2 + 3N_2\alpha + N_2\alpha + N_2 - N_2\alpha}$$

$$= \frac{3N_2(\alpha - 1) + 2N_1}{N_2(3\alpha - 2) + 2N_1}$$

$$a_{CdBr_2} = \frac{N_2(\alpha - 1) + N_1}{N_2\alpha + N_1}\left[\frac{3N_2(\alpha - 1) + 2N_1}{N_2(3\alpha - 2) + 2N_1}\right]^2 \qquad (4.88)$$

3. The complex $CdBr_2Cl_2^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdBr_2Cl_2^{2-} \rightleftharpoons Cd^{2+} + 2Br^- + 2Cl^-$$

Case 1. $2N_1 < N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1\alpha$$

$$n_{Br^-} = 2N_1\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2 - 2N_1 + 2N_1\alpha$$

$$n_{CdBr_2Cl_2^{2-}} = N_1(1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{2N_1\alpha}{2N_1\alpha + N_2 - 2N_1 + 2N_1\alpha + N_1 - N_1\alpha}$$

$$= \frac{2N_1\alpha}{N_1(3\alpha - 1) + N_2}$$

$$a_{CdBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2}\left[\frac{2N_1\alpha}{N_1\ (3\alpha - 1) + N_2}\right]^2 \qquad (4.89)$$

Case 2. $2N_1 > N_2$

At equilibrium:

$$n_{Cd^{2+}} = \tfrac{1}{2}N_2\alpha + N_1 - \tfrac{1}{2}N_2$$

$$n_{Br^-} = 2N_1 - N_2 + N_2\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2\alpha$$

$$n_{CdBr_2Cl_2^{2-}} = \tfrac{1}{2}N_2\ (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{\tfrac{1}{2}N_2\alpha + N_1 - \tfrac{1}{2}N_2}{\tfrac{1}{2}N_2\alpha + N_1 - \tfrac{1}{2}N_2 + N_2} = \frac{\tfrac{1}{2}N_2\ (\alpha - 1) + N_1}{\tfrac{1}{2}N_2\ (\alpha + 1) + N_1}$$

$$N_{Br^-} = \frac{2N_1 - N_2 + N_2\alpha}{3/2N_2\alpha - \tfrac{1}{2}N_2 + 2N_1} = \frac{N_2\ (\alpha - 1) + 2N_1}{\tfrac{1}{2}N_2\ (3\alpha - 1) + 2N_1}$$

$$a_{CdBr_2} = \frac{N_2\ (\alpha - 1) + 2N_1}{N_2\ (\alpha + 1) + 2N_1}\left[\frac{N_2\ (\alpha - 1) + 2N_1}{\tfrac{1}{2}N_2\ (3\alpha - 1) + 2N_1}\right]^2 \qquad (4.90)$$

Case 3. $2N_1 = N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1\alpha$$

$$n_{Br^-} = 2N_1\alpha$$

$$n_{Na^+} = N2$$

$$n_{Cl^-} = 2N_1\alpha$$

$$n_{CdBr_2Cl_2^{2-}} = N_1\ (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{2N_1\alpha}{N_1\ (3\alpha + 1)}$$

$$a_{CdBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2} \left[\frac{2N_1\alpha}{N_1\ (3\alpha + 1)}\right]^2 \qquad (4.91)$$

4. The complex $CdBrCl_3^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdBrCl_3^{2-} \rightleftharpoons Cd^{2+} + Br^- + 3Cl^-$$

Case 1. $3N_1 < N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1\alpha$$

$$n_{Br^-} = N_1 + N_1\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2 - 3N_1 + 3N_1\alpha$$

$$n_{CdBrCl_3^{2-}} = N1\ (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{N_1 + N_1\alpha}{N_1 + N_1\alpha + N_2 - 3N_1 + 3N_1\alpha + N_1 - N_1\alpha}$$

$$= \frac{N_1\ (\alpha + 1)}{N1\ (3\alpha - 1) + N2}$$

$$a_{CdBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2} \left[\frac{N_1\ (\alpha + 1)}{N_1\ (3\alpha - 1) + N_2}\right]^2 \qquad (4.92)$$

Case 2. $3N_1 > N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1 - {}^1/_3N_2 + {}^1/_3N_2\alpha$$

$$n_{Br^-} = 2N_1 - {}^1/_3N_2 + {}^1/_3N_2\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2\alpha$$

$$n_{CdBrCl_3^{2-}} = {}^1/_3N_2\ (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1 - {}^1/_3N_2 + {}^1/_3N_2\alpha}{N_1 - {}^1/_3N_2 + {}^1/_3N_2\alpha + N_2} = \frac{N_2\ (\alpha - 1) + 3N_1}{N_2\ (\alpha + 1) + 3N_1}$$

$$N_{Br^-} = \frac{2N_1 - {}^1/_3N_2 + {}^1/_3N_2\alpha}{2N_1 - {}^1/_3N_2 + {}^1/_3N_2\alpha + N_2\alpha + {}^1/_3N_2 - {}^1/_3N_2\alpha}$$

$$= \frac{N_2\ (\alpha - 1) + 6N_1}{3N_2\alpha + 6N_1}$$

$$a_{CdBr_2} = \frac{N_2\ (\alpha - 1) + 3N_1}{N_2\ (\alpha + 2) + 3N} \left(\frac{N_2\ (\alpha - 1) + 6N_1}{3N_2\alpha + 6N_1}\right)^2 \qquad (4.93)$$

5. The complex $CdCl_4^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdCl_4^{2-} \rightleftharpoons Cd^{2+} + 4Cl^-$$

Case 1. $4N_1 < N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1\alpha$$

$$n_{Br^-} = 2N_1$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2 - 4N_1 + 4N_1\alpha$$

$$n_{CdCl_4^{2-}} = N_1 (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{2N_1}{2N_1 + N_2 - 4N_1 + 4N_1\alpha + N_1 - N_1\alpha} = \frac{2N_1}{N_1 (3\alpha - 1) + N_2}$$

$$a_{CdBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2} \left[\frac{2N_1}{N_1 (3\alpha - 1) + N_2}\right]^2 \qquad (4.94)$$

Case 2. $4N_1 > N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha$$

$$n_{Br^-} = 2N_1$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_2\alpha$$

$$n_{CdCl_4^{2-}} = \tfrac{1}{2}N_2 (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{\tfrac{1}{2}N_2 (\alpha - 1) + N_1}{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha + N_2} = \frac{4N_1 + N_2 (\alpha - 1)}{4N_1 + N_2 (\alpha + 3)}$$

$$N_{Br^-} = \frac{2N_1}{2N_1 + N_2\alpha + \tfrac{1}{2}N_2 - \tfrac{1}{2}N_2\alpha} = \frac{8N_1}{8N_1 + N_2 (3\alpha + 1)}$$

$$a_{CdBr2} = \frac{4N_1 + N_2 (\alpha - 1)}{4N_1 + N_2 (\alpha + 3)} \left[\frac{8N_1}{8N_1 + N_2 (3\alpha + 1)}\right]^2 \qquad (4.95)$$

Calculated values for the activity of cadmium bromide at various compositions are presented in Table 4.34 and are plotted in fig. 4.22. Values for the degree of dissociation of each complex ion are also found in Table 4.34.

TABLE 4.34

System $CdBr_2$-NaCl
Values for the activity of $CdBr_2$ and the degrees of dissociation of complex ions of the form $CdX_4^{2-}$

| complex ion and relative data | mole fraction $CdBr_2$ | a(theoretical) | a(exptl.) (700°C) |
|---|---|---|---|
| $CdBr_4^{2-}$ | 0.10 | 0.0024 | 0.003 |
| Ref. pt. $N_1 = 0.5$ | 0.20 | 0.0167 | 0.019 |
| $a_1 = 0.183$ | 0.30 | 0.0496 | 0.050 |
| $\alpha = 0.86$ | 0.40 | 0.105 | 0.108 |
| | 0.50 | 0.183 | 0.207 |
| | 0.60 | 0.285 | 0.319 |
| | 0.70 | 0.411 | 0.453 |
| | 0.80 | 0.560 | 0.784 |
| | 0.90 | 0.731 | 0.860 |
| $CdBr_3Cl^{2-}$ | 0.10 | 0.0023 | 0.003 |
| Ref. pt. $N_1 = 0.4$ | 0.20 | 0.0161 | 0.019 |
| $a_1 = 0.105$ | 0.30 | 0.049 | 0.050 |
| $\alpha = 0.845$ | 0.40 | 0.104 | 0.108 |
| | 0.50 | 0.187 | 0.207 |
| | 0.59 | 0.283 | 0.319 |
| | 0.70 | 0.447 | 0.453 |
| | 0.80 | 0.619 | 0.784 |
| $CdBr_2Cl_2^{2-}$ | 0.10 | 0.0022 | 0.003 |
| Ref. pt. $N_1 = 0.3$ | 0.20 | 0.0159 | 0.019 |
| $a_1 = 0.05$ | 0.30 | 0.0499 | 0.050 |
| $\alpha = 0.835$ | 0.33 | 0.067 | 0.065 |
| | 0.40 | 0.116 | 0.108 |
| | 0.50 | 0.213 | 0.207 |
| | 0.60 | 0.335 | 0.319 |
| | 0.70 | 0.478 | 0.453 |
| | 0.80 | 0.638 | 0.784 |
| | 0.90 | 0.813 | 0.860 |

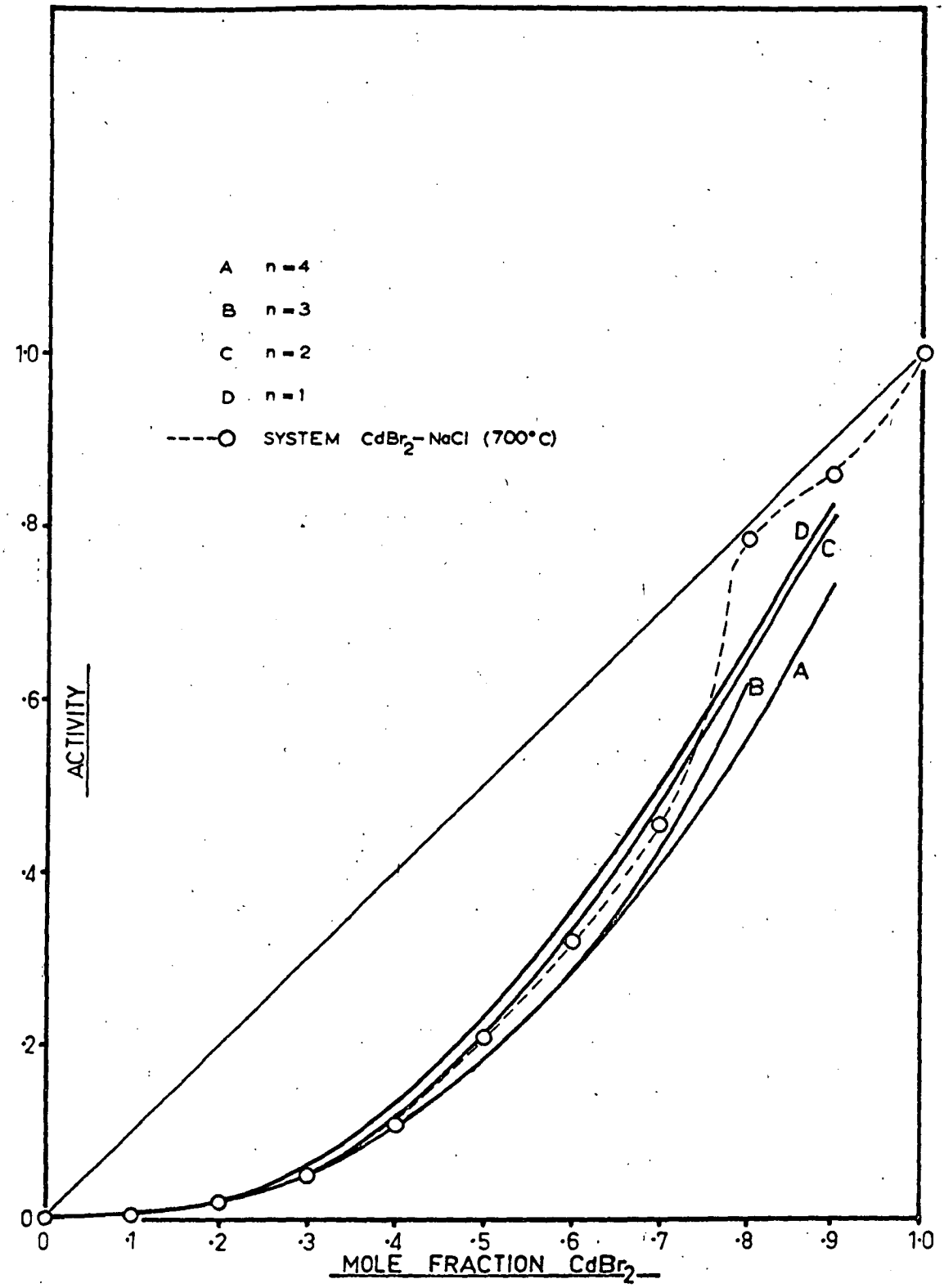



FIG. 4·22 THEORETICAL ACTIVITIES OF $CdBr_2$ ASSUMING COMPLEX IONS OF THE FORM $CdBr_nCl^{2-}_{(4-n)}$ FOR THE SYSTEM $CdBr_2$–NaCl

Table 4.34 (contd.)

| complex ion and relative data | mole fraction $CdBr_2$ | a(theoretical) | a(exptl.) (700°C) |
|---|---|---|---|
| $CdCl_4^{2-}$ | 0.10 | 0.0021 | 0.003 |
| Arbitrary value | 0.20 | 0.0169 | 0.019 |
| of $\alpha$ = 0.8 | 0.30 | 0.059 | 0.050 |
| | 0.40 | 0.113 | 0.108 |
| | 0.50 | 0.238 | 0.207 |
| | 0.60 | 0.357 | 0.319 |
| | 0.70 | 0.498 | 0.453 |
| | 0.80 | 0.655 | 0.784 |
| | 0.90 | 0.823 | 0.860 |
| | No value of $\alpha$ was found as the complex $CdCl_4^{2-}$ produces no deviations of $a_{CdBr_2}$ which are negative with respect to the ideal Temkin line over the range of composition investigated. Hence no value of $a_{CdBr_2}$ was estimated. | | |

(ii) The system $CdCl_2$-NaBr

1. The complex $CdCl_4^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdCl_4^{2-} \rightleftharpoons Cd^{2+} + 4Cl^-$$

The following calculation applies over the whole composition range.

At equilibrium:

$$n_{Cd^{2+}} = \tfrac{1}{2}N_1 + \tfrac{1}{2}N_1\alpha$$

$$n_{Br^-} = N_2$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1\alpha$$

$$n_{CdCl_4^{2-}} = \tfrac{1}{3}N_1 (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{\tfrac{1}{3}N_1 (1 + \alpha)}{\tfrac{1}{3}N_1 (1 + \alpha) + N_2} = \frac{N_1 (1 + \alpha)}{N_1 (1 + \alpha) + 2N_2}$$

$$N_{Br^-} = \frac{N_2}{N_2 + 2N_1\alpha + \tfrac{1}{3}N_1 - \tfrac{1}{3}N_1\alpha} = \frac{2N_2}{2N_2 + N_1 (3\alpha + 1)}$$

$$a_{CdBr_2} = \frac{N_1 (1 + \alpha)}{N_1 (1 + \alpha) + 2N_2} \left[\frac{2N_2}{2N_2 + N_1 (3\alpha + 1)}\right]^2 \qquad (4.96)$$

$\alpha = 1$, $a_{CdBr_2}$ = Temkin model value

$$\alpha = 0, \; a_{CdBr_2} = \frac{N_1}{N_1 + 2N_2} \left[\frac{2N_2}{2N_2 + N_1}\right]^2 \qquad (4.97)$$

2. The complex $CdBrCl_3^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdBrCl_3^{2-} \rightleftharpoons Cd^{2+} + Br^- + 3Cl^-$$

Case 1. $2N_1 < 3N_2$

At equilibrium:

$$n_{Cd^{2+}} = {}^1/_3N_1 + {}^2/_3N_1\alpha$$

$$n_{Br^-} = N_2 - {}^2/_3N_1 + {}^2/_3N_1\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1\alpha$$

$$n_{CdBrCl_3^{2-}} = {}^2/_3N_1 (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{{}^1/_3N_1 + {}^2/_3N_1\alpha}{{}^1/_3N_1 + {}^2/_3N_1\alpha + N_2} = \frac{N_1 (1 + 2\alpha)}{N_1 (1 + 2\alpha) + 3N_2}$$

$$N_{Br^-} = \frac{N_2 - {}^2/_3N_1 + {}^2/_3N_1\alpha}{N_2 - {}^2/_3N_1 + {}^2/_3N_1\alpha + 2N_1\alpha + {}^2/_3N_1 - {}^2/_3N_1\alpha}$$

$$= \frac{3N_2 + 2N_1\ (\alpha - 1)}{3N_2 + 6N_1\alpha}$$

$$a_{CdBr_2} = \frac{N_1\ (1 + 2\alpha)}{N_1\ (1 + 2\alpha) + 3N_2} \left[\frac{3N_2 + 2N_1\ (\alpha - 1)}{3N_2 + 6N_1\alpha}\right]^2 \qquad (4.98)$$

$\alpha = 1$, $a_{CdBr_2}$ = Temkin model activity

$$\alpha = 0,\ a_{CdBr_2} = \frac{N_1}{N_1 + 3N_2} \left[\frac{3N_2 - 2N_1}{3N_2}\right]^2 \qquad (4.99)$$

Case 2. $2N_1 > 3N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1 - N_2 + N_2\alpha$$

$$n_{Br^-} = N_2\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1 - 3N_2 + 3N_2\alpha$$

$$n_{CdBrCl_3^{2-}} = N_2\ (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1 - N_2 + N_2\alpha}{N_1 - N_2 + N_2\alpha + N_2} = \frac{N_1 + N_2\ (\alpha - 1)}{N_1 + N_2\alpha}$$

$$N_{Br^-} = \frac{N_2\alpha}{N_2\alpha + 2N_1 - 3N_2 + 3N_2\alpha + N_2 - N_2\alpha}$$

$$= \frac{N_2\alpha}{2N_1 + N_2\ (3\alpha - 2)}$$

$$a_{CdBr_2} = \frac{N_1 + N_2\ (\alpha - 1)}{N_1 + N_2\alpha} \left[\frac{N_2\alpha}{2N_1 + N_2\ (3\alpha - 2)}\right]^2 \qquad (4.100)$$

$\alpha = 1$, $a_{CdBr_2}$ = Temkin model activity

$\alpha = 0$, $a_{CdBr_2} = 0$ (4.101)

### 3. The complex $CdBr_2Cl_2^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdBr_2Cl_2^{2-} \rightleftharpoons Cd^{2+} + 2Br^- + 2Cl^-$$

**Case 1.** $2N_1 < N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1\alpha$$

$$n_{Br^-} = N_2 - 2N_1 + 2N_1\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1\alpha$$

$$n_{CdBr_2Cl_2^{2-}} = N_1 (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{N_2 - 2N_1 + 2N_1\alpha}{N_2 - 2N_1 + 2N_1\alpha + 2N_1\alpha + N_1 - N_1\alpha}$$

$$= \frac{N_2 - 2N_1 (\alpha - 1)}{N_2 + N_1 (3\alpha - 1)}$$

$$a_{CdBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2} \left[\frac{N_2 + 2N_1 (\alpha - 1)}{N_2 + N_1 (3\alpha - 1)}\right]^2 \qquad (4.102)$$

$\alpha = 1$, $a_{CdBr_2}$ = Temkin model value

$\alpha = 0$, $a_{CdBr_2} = 0$ (4.103)

**Case 2.** $2N_1 > N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha$$

$$n_{Br^-} = N_2\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1 - N_2 + N_2\alpha$$

$$n_{CdBr_2Cl_2^{2-}} = \tfrac{1}{2}N_2\,(1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha}{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha + N_2} = \frac{2N_1 + N_2\,(\alpha - 1)}{2N_1 + N_2\,(\alpha + 1)}$$

$$N_{Br^-} = \frac{N_2\alpha}{N_2\alpha + 2N_1 - N_2 + N_2\alpha + \tfrac{1}{2}N_2 - \tfrac{1}{2}N_2\alpha}$$

$$\frac{2N_2\alpha}{4N_1 + N_2\,(3\alpha - 1)}$$

$$a_{CdBr_2} = \frac{2N_1 + N_2\,(\alpha - 1)}{2N_1 + N_2\,(\alpha + 1)} \left[\frac{2N_2\alpha}{4N_1 + N_2\,(3\alpha - 1)}\right]^2 \qquad (4.104)$$

$\alpha = 1$, $a_{CdBr_2}$ = Temkin model value

$\alpha = 0$, $a_{CdBr_2} = 0$ (4.105)

4. The complex $CdBr_3Cl^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdBr_3Cl^{2-} \rightleftharpoons Cd^{2+} + 3Br^- + Cl^-$$

Case 1. $3N_1 < N_2$

At equilibrium:

$$n_{Cd^{2+}} = N1\alpha$$

$$n_{Br^-} = N_2 - 3N_1 + 3N_1\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = N_1 + N_1\alpha$$

$$n_{CdBr_3Cl^{2-}} = N_1\,(1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1 \alpha}{N_1 \alpha + N_2}$$

$$N_{Br^-} = \frac{N_2 - 3N_1 + 3N_1 \alpha}{N_2 - 3N_1 + 3N_1 \alpha + N_1 + N_1 \alpha + N_1 - N_1 \alpha}$$

$$= \frac{N_2 + 3N_1 (\alpha - 1)}{N_2 + N_1 (3\alpha - 1)}$$

$$a_{CdBr_2} = \frac{N_1 \alpha}{N_1 \alpha + N_2} \left[ \frac{N_2 + 3N_1 (\alpha - 1)}{N_2 + N_1 (3\alpha - 1)} \right]^2 \qquad (4.106)$$

$\alpha = 1$, $a_{CdBr_2}$ = Temkin model value

$\alpha = 0$, $a_{CdBr_2} = 0$ (4.107)

Case 2. $3N_1 > N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1 - {}^1/_{3N_2} + {}^1/_{3N_2 \alpha}$$

$$n_{Br^-} = N_2 \alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1 - {}^1/_{3N_2} + {}^1/_{3N_2 \alpha}$$

$$n_{CdBr_3Cl^{2-}} = {}^1/_{3N_2} (1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1 - {}^1/_{3N_2} + {}^1/_{3N_2 \alpha}}{N_1 - {}^1/_{3N_2} + {}^1/_{3N_2 \alpha} + N_2} = \frac{3N_1 + N_2 (\alpha - 1)}{3N_1 + N_2 (\alpha + 2)}$$

$$N_{Br^-} = \frac{N_2 \alpha}{N_2 \alpha + 2N_1 - {}^1/_{3N_2} + {}^1/_{3N_2 \alpha} - {}^1/_{3N_2 \alpha} + {}^1/_{3N_2}}$$

$$= \frac{N_2 \alpha}{N_2 \alpha + 2N_1}$$

$$a_{CdBr_2} = \frac{3N_1 + N_2 (\alpha - 1)}{3N_1 + N_2 (\alpha + 2)} \left[ \frac{N_2 \alpha}{N_2 \alpha + 2N_1} \right]^2 \qquad (4.108)$$

$$\alpha = 1,\ a_{CdBr_2} = \text{Temkin model activity}$$

$$\alpha = 0,\ a_{CdBr_2} = 0 \qquad (4.109)$$

5. The complex $CdBr_4^{2-}$

Let the following scheme be representative of the dissociation of the complex ion:

$$CdBr_4^{2-} \rightleftharpoons Cd^{2+} + 4Br^-$$

Case 1. $4N_1 < N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1\alpha$$

$$n_{Br^-} = N_2 - 4N_1 + 4N_1\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1$$

$$n_{CdBr_4^{2-}} = N_1 ( 1 - \alpha)$$

$$N_{Cd^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{N_2 - 4N_1 + 4N_1\alpha}{N_2 - 4N_1 + 4N_1\alpha + N_2} = \frac{N_2 + 4N_1\ (\alpha - 1)}{2N_2 + 4N_1\ (\alpha - 1)}$$

$$a_{CdBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2} \left[\frac{N_2 + 4N_1\ (\alpha - 1)}{2N_2 + 4N_1\ (\alpha - 1)}\right]^2 \qquad (4.110)$$

$$\alpha = 1,\ a_{CdBr_2} = \text{Temkin model value} \qquad (4.111)$$

$$\alpha = 0,\ a_{CdBr_2} = 0$$

Case 2. $4N_1 > N_2$

At equilibrium:

$$n_{Cd^{2+}} = N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha$$

$$n_{Br^-} = N_2\alpha$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1$$

$$n_{CdBr_4^{2-}} = \tfrac{1}{2}N_2\,(1-\alpha)$$

$$N_{Cd^{2+}} = \frac{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha}{N_1 - \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2\alpha + N_2} = \frac{4N_1 + N_2\,(\alpha - 1)}{4N_1 + N_2\,(\alpha + 3)}$$

$$N_{Br^-} = \frac{N_2\alpha}{N_2\alpha + 2N_1 + \tfrac{1}{2}N_2 - \tfrac{1}{2}N_2\alpha} = \frac{4N_2\alpha}{8N_1 + N_2\,(3\alpha + 1)}$$

$$a_{CdBr_2} = \frac{4N_1 + N_2\,(\alpha - 1)}{4N_1 + N_2\,(\alpha + 3)} \left[\frac{4N_2\alpha}{8N_1 + N_2\,(3\alpha + 1)}\right]^2 \qquad (4.112)$$

$\alpha = 1$, $a_{CdBr_2}$ = Temkin model activity

$\alpha = 0$, $a_{CdBr_2} = 0$ (4.113)

Case 3. $4N_1 = N_2$

At equilibrium

$$n_{Cd^{2+}} = N_1\alpha$$

$$n_{Br^-} = 4N_1\alpha\ (= N_2\alpha)$$

$$n_{Na^+} = N_2$$

$$n_{Cl^-} = 2N_1$$

$$n_{CdBr_4^{2-}} = N_1\,(1-\alpha)$$

$$N_{Cd^{2+}} = \frac{N_1\alpha}{N_1\alpha + N_2}$$

$$N_{Br^-} = \frac{4N_1\alpha}{4N_1\alpha + 2N_1 + N_1 - N_1\alpha} = \frac{4\alpha}{3(1+\alpha)}$$

$$a_{CdBr_2} = \frac{N_1\alpha}{N_1\alpha + N_2}\left[\frac{4\alpha}{3(1+\alpha)}\right]^2 \qquad (4.114)$$

$$\alpha = 1,\ a_{CdBr_2} = \text{Temkin model activity} \qquad (4.115)$$

$$\alpha = 0,\ a_{CdBr_2} = 0$$

Calculated values for the activity of cadmium bromide at various compositions are presented in Table 4.35 and are plotted in fig. 4.23. Values for the degree of dissociation of each complex ion are also found in Table 4.35.

(iii) Discussion of model applied to both systems

For both reciprocal systems, activity values, calculated on the basis of the postulate of the presence of complex ions $CdBr_4^{2-}$ and $CdBr_3Cl^{2-}$ in the molten mixtures, show least discrepancy with experimental values. It is deduced therefore, that on the basis of this model, $CdBr_4^{2-}$ and $CdBr_3Cl^{2-}$ are the complex ions which, of all the ions considered, are most likely to be present in the mixtures.

For the system $CdBr_2$-NaCl, the model which assumes the species $CdBr_4^{2-}$ gives very good agreement up to about 0.55 mole fraction $CdBr_2$. Thereafter the experimental curve shows a considerable positive deviation, which for compositions in excess of 55 mole % $CdBr_2$, is attributed to the greater tendency for cadmium bromide "molecules" to dissociate. Apart from the activity model assuming the ion $CdBr_3Cl^{2-}$, which shows equally good agreement between $a_{CdBr_2}$ (exptl.) and $a_{CdBr_2}$ (theoretical) over the same composition range, the models

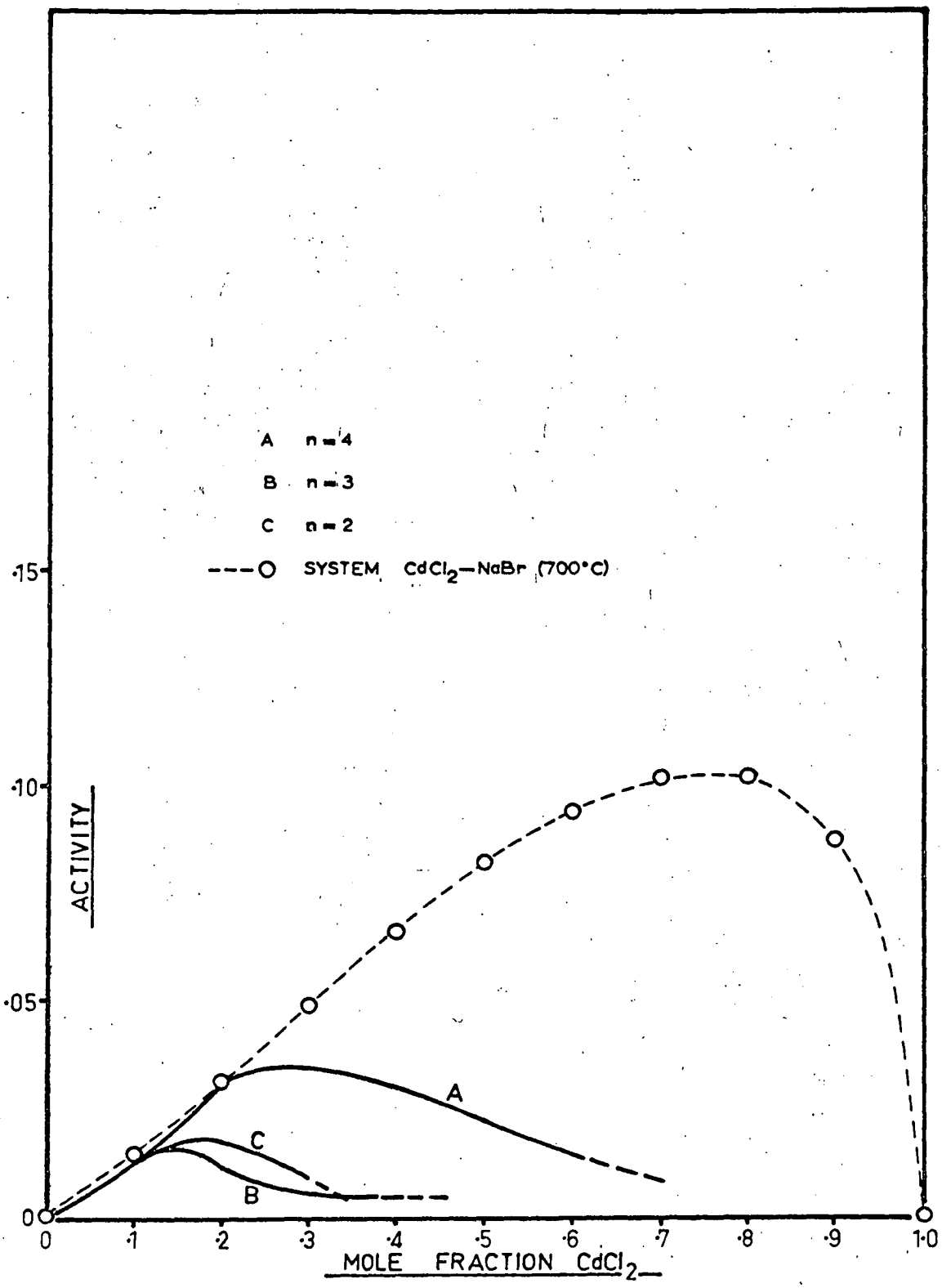



FIG. 4·23 THEORETICAL ACTIVITIES OF $CdBr_2$ ASSUMING COMPLEX IONS OF THE FORM $CdBr_n Cl_{(4-n)}^{2-}$ FOR THE SYSTEM $CdCl_2$—NaBr

TABLE 4.35

System $CdCl_2$-NaBr
Values for the activity of cadmium bromide and the degree of dissociation of complex ions of the form $CdX_4^{2-}$

| complex ion and relative data | mole fraction $CdCl_2$ | a(theoretical) | a(exptl.) (700°C) |
|---|---|---|---|
| $CdCl_4^{2-}$, $CdCl_3Br^{2-}$ | These complex ions do not contribute to $a_{CdBr_2}$ sufficiently to give deviations to match the experimental curve, even when $\alpha = 0$ | | |
| $CdBr_2Cl_2^{2-}$ | 0.10 | 0.014 | 0.015 |
| Ref. pt. $N_1 = 0.1$ | 0.20 | 0.018 | 0.0315 |
| $a_1 = 0.014$ | 0.30 | 0.009 | 0.049 |
| $\alpha = 0.17$ | | | |
| $CdBr_3Cl^{2-}$ | 0.10 | 0.0148 | 0.015 |
| Ref. pt. $N_1 = 0.1$ | 0.20 | 0.0114 | 0.0315 |
| $a_1 = 0.014$ | 0.30 | 0.0066 | 0.049 |
| $\alpha = 0.23$ | 0.40 | 0.0063 | 0.066 |
| $CdBr_4^{2-}$ | 0.10 | 0.0122 | 0.015 |
| Ref. pt. $N_1 = 0.2$ | 0.20 | 0.0303 | 0.0315 |
| $a_1 = 0.031$ | 0.30 | 0.0346 | 0.049 |
| $\alpha = 0.58$ | 0.40 | 0.0297 | 0.066 |
| | 0.50 | 0.0221 | 0.082 |
| | 0.60 | 0.0144 | 0.094 |

assuming species containing a higher proportion of chlorine, give poor agreement for most mixtures.

For the system $CdCl_2$-NaBr, of all the complex ions possible, the model assuming the complex ion $CdBr_4^{2-}$ gives the best agreement between experimental and theoretical activities for $CdBr_2$. However, the agreement is reasonable over a small range of composition only.

Although the proposed model for estimating the activities of $CdBr_2$ on the assumption of complex ion formation, gives the best agreement with the experimentally determined activity over relatively large composition ranges (compared to the other models), it is still, nevertheless, inadequate for the following reasons:

(1) The actual range of composition over which the model is applicable is small for the system $CdCl_2$-NaBr.

(2) The model is inapplicable to solutions containing high proportions of $CdBr_2$ and $CdCl_2$. The deviations of the activity of $CdBr_2$ for these composition ranges are attributed to the dissociation of $CdBr_2$ and $CdCl_2$ "molecules". In this case a different model for $a_{CdBr_2}$ may apply; for example, a model based on the dissociation scheme $CdX_2 \rightleftharpoons Cd^{2+} + 2X^-$, may be proposed.

(3) The values of $\alpha$, calculated for similar complex ions in the systems $CdBr_2$-NaCl and $CdCl_2$-NaBr, are very different. For similar mole fractions of $CdX_2$, the stability of a given complex ion will be slightly influenced by the different environments in the two systems; therefore a slight variation in $\alpha$ will result. However, large differences in the degree of dissociation of, for example, the ion $CdBr_3Cl^{2-}$, in the two systems ($\alpha$ = 0.845 for the system $CdBr_2$-NaCl and $\alpha$ = 0.23 for the system $CdCl_2$-NaBr), suggest that either the model is inapplicable, or else the complex ion $CdBr_3Cl^{2-}$ does not contribute to the experimental deviations of $a_{CdBr_2}$ from the Temkin activity. The agreement between $\alpha$, for the ion $CdBr_4^{2-}$ in the two systems is,

however, much closer ( $\alpha$ = 0.86 for the system $CdBr_2$-NaCl and $\alpha$ = 0.58 for the system $CdCl_2$-NaBr).

It is felt therefore, that the model for the activity of $CdBr_2$, assuming the complex ion $CdBr_4^{2-}$, applies for mixtures of $CdBr_2$ and NaCl, and $CdCl_2$ and NaBr, containing a high proportion of alkali metal halide, but is inadequate for other mixtures.

## SECTION D

## SUMMARY

The thermodynamic properties of the divalent metal halides ($AX_2$), can be explained in terms of complex ion formation and association of the standard state. The variation of $a_{AX_2}$ with increasing temperature can be attributed to two opposing effects: (a) dissociation of co-valent complex ions and ionic associations due to increased thermal vibration, and (b) increase in the tendency to form ion pairs; the nature of the alkali metal ion present determines the more dominant effect.

In the systems $PbBr_2$-RbBr, and $PbBr_2$-CsBr for solutions rich in the alkali halide, the most predominant complex ion is likely to be $PbBr_6^{4-}$, with the ions $PbBr_4^{2-}$ and $PbBr_3^-$ present to lesser extents. For the system $PbBr_2$-KBr, the most predominant ion is likely to be $PbBr_4^{2-}$. As the radius of the alkali metal ion becomes smaller however, the four and three co-ordinated ions become of greater importance. Of the activity models proposed for these systems, the Hildebrand and stepwise complex formation models give the best agreement with experiment; the latter is regarded as having the greatest potential as a model.

The partial thermodynamic quantities of $PbCl_2$ in the three component systems $PbCl_2$-CsCl-MCl (where M = Li, Na, K, Rb), have been discussed in terms of the relative polarizing influence of the two alkali metal cations $Cs^+$ and $M^+$. This has resulted in a classification of the alkali metal cations into two groups, i.e., $Li^+$, $Na^+$ and $K^+$, $Rb^+$, $Cs^+$. The presence of the former drastically reduces the stability of complex ions of the form $PbCl_n^{(n-2)-}$, whereas the latter have little effect. The activity model proposed, shows reasonable agreement

with the experimental results for $a_{PbCl_2}$ in these systems.

The reciprocal systems $CdBr_2$-NaCl and $CdCl_2$-NaBr, are complicated by complex ion formation, appreciable association of the standard state, as well as the exchange reaction between cations and anions. The deviations of $a_{CdBr_2}$ from the Temkin activity have been attributed to the presence of complex ions (of the type $CdX_4^{2-}$) and undissociated $CdCl_2$ and $CdBr_2$ "molecules". Previous activity models for reciprocal molten salt mixtures are found to be inapplicable but the proposed model gives reasonable agreement with experiment, for mixtures containing excess of alkali halide.

# AUTHOR INDEX

# AUTHOR INDEX

(alphabetical list of authors and the page numbers where references are quoted)

## ACKNOWLEDGMENTS

The author wishes to thank Professor H. Bloom for his invaluable help and suggestions during the course of this work and members of the Chemistry Department for their helpful discussions. The author also wishes to thank the University of Tasmania for the award of a University Research Studentship.